HYPERFINE STRUCTURE IN
LINE SPECTRA AND NUCLEAR SPIN

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TOLANSKY, S.	HYPERFINE STRUCTURE IN LINE SPECTRA AND NUCLEAR SPIN
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HYPERFINE STRUCTURE IN LINE SPECTRA AND NUCLEAR SPIN

by

S. TOLANSKY
D.Sc., Ph.D., D.I.C.

WITH 29 DIAGRAMS

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PREFACE TO THE SECOND EDITION

DURING the twelve years that have passed since the writing of the first edition, considerable advances have been made both in the theoretical and experimental aspects of the study of hyperfine structure in line spectra. This has of necessity resulted in a good deal of re-writing in the preparing of a second edition. Chapters I, II, VIII, X, XI, and XII are largely new, the other chapters being modified mainly in details.

Nuclear spins are now known for 55 different atoms, including among them 79 isotopic species, and for 65 of these, nuclear magnetic moments have been determined. These relatively large numbers enable an approximate statistical approach to be made, but it cannot yet be said that theories of the origin of either nuclear spin or nuclear magnetic moment are out of the hypothetical stage. Although a number of such theories have of course been proposed, it is considered that as yet they are not sufficiently developed to be included in an introductory book such as this.

As far as possible, however, nuclear data have been brought up to date. References have been omitted in compiling the tables of moments, since the data have been compiled from a considerable number of original papers and a cumbersome list would be out of place.

A brief chapter has been added dealing with nuclear electrical quadrupole moment, since this promises to be of especial future importance. Isotope effects are treated more comprehensively than formerly.

<div style="text-align: right">S. TOLANSKY</div>

MANCHESTER, *January*, 1946

PREFACE

This book is meant as an introduction to the study of fine structure in line spectra for those who are already familiar with the elements of spectroscopy. The study of fine structure has already led to many important facts concerning the constitution of atomic nuclei, and will certainly lead to more. It is hoped that this short survey will prove useful to the student who contemplates undertaking research in this branch of the subject. The experimental and theoretical material is accumulating at a very rapid rate, so that no claim to completeness can be made, but the more important facts known up to date have been included. It has not been considered advisable, because of lack of space, to treat the Zeeman effect in detail, so that only a brief summary is given in an appendix.

I take this opportunity of expressing my thanks to Dr. W. E. Williams of King's College, London, who has completely revised the manuscript and made many valuable and helpful suggestions.

I also wish to thank Miss E. Pincasovitch, who has kindly executed all the diagrams for me.

S. T.

IMPERIAL COLLEGE OF SCIENCE,
LONDON, *February*, 1935

CONTENTS

APPENDICES

CHAPTER I

INTRODUCTION

IT is now some fifty years since spectroscopists first found
that some of the lines of the spectra of a number of elements
were in reality complex close line groups. This complex
close structure, revealed only by instruments of high dis-
persion and high resolution, was formerly called "fine
structure" but for sound reasons this terminology has
generally now been replaced by "hyperfine structure".

With improvements in technique, it has now been estab-
lished that in many spectra the majority of the lines are
complex. Such a complex usually consists of a small
number of components, rarely exceeding perhaps a dozen,
and often with no apparent easily recognised regularity
within the complex pattern. These hyperfine structures,
for long a puzzle, assumed considerable importance when
it was recognised that atomic *nuclear* properties are respon-
sible for their appearance and at once a new and powerful
method for studying atomic nuclei was developed. It has
been established beyond all doubt that these hyperfine
structures are due either to (a) isotopic mixtures or (b) spin
properties of the atomic nuclei.

As a result of extensive spectroscopic investigation, im-
portant contributions to our knowledge of atomic nuclei
have been made. The physics of the nucleus has become
a study of fundamental importance, and recent develop-
ments, such as the evolution of the atomic bomb, based on
nuclear fission, point to the bigger and bigger place that
nuclear physics will hold.

There are available perhaps some five broadly distinct
experimental methods for studying nuclear properties.
Taking them historically, these are (a) Radioactive, (b)
Spectroscopic, (c) Magnetic, (d) Collision-disintegrative,
(e) Cosmic rays.

Radioactive experiments first established the nuclear
structure of the atom and revealed details about nuclear

structure, nuclear energy levels and nuclear constituent particles. Leaving for later the discussion of the spectroscopic methods, the magnetic technique, whilst limited in application, is of very high precision. It is found that a jet of atoms, when passing through a non-uniform magnetic field, suffers deflection which, when interpreted, yields the mechanical and magnetic spin properties of the nuclei of the atoms constituting the jet. This magnetic method correlates very closely with the spectroscopic method.

So important and well known are the collision-disintegration experiments made with both natural radioactive projectiles and with accelerated particles from machines like cyclotrons, that little need be said about the fundamental discoveries and contributions made by this study. Cosmic ray experiments have contributed in a very fundamental way to the study of the nucleus and one need but mention the discoveries of the positron and meson to realise this.

The purpose of this book is to discuss one aspect of the lesser known spectroscopic method of approach, namely that of hyperfine structure in line spectra and it will be shown that not only has a great deal already been found by this technique, but that there is considerable future scope in addition.

Two distinct spectroscopic methods for investigating problems of nuclear structure have been developed. The first method involves the difficult measurement of the alternations in intensity found in the rotation lines of many molecular band spectra. The simplest type of molecule is of the homogeneous kind consisting of two similar molecules such as O_2 or N_2. A homogeneous molecule is one in which the constituent atoms are of the same isotopic species, e.g. O_{16-16}, (but not O_{16-17}). When such a homogeneous molecule emits an electronic band spectrum, alternate rotation lines of the band bear a fixed ratio to one another. It can be shown on theoretical grounds that the alternation of intensity arises because of a nuclear spin, the spin being characteristic for the particular constituent atoms forming the molecule. . Each nucleus has a *mechanical* spin moment which is some small integral or half integral, multiple of

$h/2\pi$, h being Planck's constant. The intensity ratio depends, then, upon the number I (called the nuclear spin) where $I \cdot \dfrac{h}{2\pi}$ is the mechanical moment. This ratio is $\dfrac{(I + 1)}{I}$.

The intensity ratio arises as a purely statistical effect, alternate transitions being more probable than their neighbouring transitions by virtue of the mechanical moment.

It can be shown by various methods that the mechanical moment of the hydrogen nucleus (this is a single proton) is $\frac{1}{2} \cdot \left(\dfrac{h}{2\pi} \right)$ and it is now considered probable that an I greater than $\frac{9}{2}$ for stable atomic nuclei in unexcited states is not found. The relatively small values of I, especially in heavy atoms containing some two hundred particles, is an indication that possibly only a small fraction of the nucleus is involved in the spin property.

Since the nucleus is electrically charged, one expects that the mechanical spin will produce an associated magnetic moment, which indeed it does. (It will be shown later that even *uncharged* spinning nuclear particles can produce also a magnetic moment.) This nuclear magnetic moment couples with any other electronic magnetic moment of the atom. Each valency electron, which is involved in the production of the line spectrum, has a magnetic moment and this couples with the nuclear magnetic moment. As a result, the spectroscopic levels characteristic of the valency electrons are split up into a number of sub-levels.

The magnetic moment of the proton, being inversely as the mass, is some two thousand times smaller than that of the electron. Now, as will be indicated later, the separation of lines of a multiplet in a spectrum depend largely upon the spin magnetic moment of the electron. The separations due to nuclear spin are thus considerably smaller than those due to electron spin, hence the use of the term " hyperfine structure " to distinguish this splitting from " gross multiplet structure ", sometimes called " fine structure ".

It is clear now why the study of hyperfine structure can be expected to reveal information both about nuclear mechanical and nuclear magnetic moments. But recent work has revealed much more. Interesting isotope effects have been discovered, the statistical distribution of nuclear spins has proved to be of value, and unsymmetry in nuclear electrical charge distribution has been demonstrated.

The measurement of hyperfine structure presents a number of particular experimental difficulties due in the first place to the minute scale of the structures. Most readers will be familiar with the close doublet gross structure multiplet separation of the sodium D lines, usually just separated by typical small dispersion instruments. The wave number separation for this doublet is of the order 25 cm.$^{-1}$ (some 6 angstrom units). Taking this as a standard, the problems involved will be realised when it is noted that hyperfine structures of 0·010 cm.$^{-1}$ are commonly met with and much smaller structures occur and are detectable only with the most refined techniques.

There are two experimental problems, namely the development of suitable line sources and the employment of high resolution instruments. This experimental aspect is being treated by the writer in a separate and much more comprehensive treatise.[1] The salient features will be briefly reviewed in the next chapter, which will deal with line width, sources and instruments.

REFERENCE

[1] Tolansky, " High Resolution Spectroscopy " (Methuen).

EXPERIMENTAL TECHNIQUE

RAPID advances in hyperfine structure studies only took place when it was recognised that special spectroscopic sources were needed before existing high resolution instruments could be brought to bear. In general, the separate components of a hyperfine structure complex lie very close together and care must be taken to employ sources in which the widths of spectrum lines are small compared with the separations of the components. This is an obvious statement, for if the natural width of a component is greater than, or even only of the same order as, the separation between it and its neighbours, the overlapping members can never be resolved, no matter how powerful the observing instrument may be.

It so happens that all existing instruments of high dispersion and high resolution require intense light sources and this introduces a serious complication, for, in general, those procedures adopted for increasing brilliancy usually simultaneously increase line width and it may be crudely considered that line brilliance and line sharpness are mutually contradictory. For example, a hot arc in air (a brilliant source) can produce line widths of o·5 cm.$^{-1}$ or more, condensed electric discharge often leads to line widths ten times this, high pressure arc line widths can be one hundred times this, etc. The application of high resolution instruments to such lines is useless. Line sharpness is the prime consideration and we shall consider the factors contributory to line width.

Natural or radiation width

Quantum mechanics has shown that each line transition has a natural, usually very small, line width, which owes its origin to the fact that any spectroscopic level is not

infinitely narrow in terms of energy, but occupies a definite band of energy depending upon the average time the electron remains in the particular level involved.   This natural line width is usually far too small to be of significance.   In special cases, however, one term of a line can interact with another region of continuous energy.   In this case the width is so great that the line broadens out into almost a continuum, with the result that all hyperfine study is excluded.

Doppler width

This is one of the few causes seriously affecting equally both emission and absorption lines.   Atoms which emit (absorb) light have different velocities of thermal agitation, corresponding to a Maxwellian distribution curve.   Let all the atoms inherently emit light of the same wavelength. The effective wavelength observed from those atoms moving towards an observer is diminished and for those atoms moving away it is increased, in accordance with Doppler's principle.   The result clearly is a line broadening, the line shape have a Maxwellian distribution.

Defining the half width W as the width of the line at half the peak intensity, it can be shown that, closely enough

$$W = 10^{-6} \sqrt{\frac{T}{M}}\, \nu \text{ cm.}^{-1}$$

where ν is the wave number of the line, T is the absolute temperature of emission and M the mass of the emitter.

For an arc at 3600° Abs. a line at λ 5000 given out by an emitter of mass = 1, has a line width of 1·2 cm.$^{-1}$. Clearly such a line width is prohibitive and drastic cooling must be adopted (usually liquid air).   For M large (say mercury) such cooling is not always essential.

Pressure broadening

This effect depends upon the nature, density and temperature of the gas wherein the radiating or absorbing atom is situated.   Such an atom is subject to perturbation forces

produced by any closely approaching neighbouring atoms. In absorption observations these are neutral, but in emission some will be charged. Highly complex effects result, leading to effective term broadening increasing proportional to the pressure and depending in a very marked way on the nature of the perturbing gas. Typical collision broadenings in atmospheric pressure arcs are of the order of 0·4 to 1·0 cm.$^{-1}$. To reduce these effects, pressures below 1 mm. are desirable.

Resonance broadening

This is a particularly severe form of pressure broadening, which sets in when the perturbing atoms are of the same kind as the emitter, e.g. sodium in sodium vapour as distinct from sodium in, say, nitrogen gas. At a pressure of 0·2 mm. of sodium vapour the resonance width of the D lines is 0·6 cm.$^{-1}$, which is one hundred times that produced by the same pressure of foreign gas.

Stark effect broadening

When emitting or absorbing atoms are in a strong uniform electric field, spectral levels are split up and the lines become complex narrow groups, the extent of the pattern, according to circumstances, being proportional to either the field strength or to its square. A non-uniform field leads to an effective line broadening. In bad cases a field of only 1000 volts/cm. can lead to line broadening of some cm.$^{-1}$. The remedy is to reduce the effective field in the region of emission.

Interatomic stark broadening is a related effect produced by local fields set up by ion concentrations. It is clear that powerful currents and condensed discharges always lead to prohibitive line broadening and must therefore be avoided. This feature has been a principal factor in stimulating the development of special sources.

Self reversal broadening

When radiation from a hot gas passes through a cooler layer of the same vapour, the central portion of the emission

line is preferentially absorbed. The amount of absorption
depends upon the absorption coefficient and on the square
root of the total number of absorbing atoms in the line of
sight.   A 20 cm. length of path in sodium vapour at a pres-
sure of 0·01 mm. (300° C.) leads to a line width of some
2 cm.$^{-1}$.

When the central absorption becomes pronounced, a
spurious doublet results, as shown in Fig. 1. In Fig. 1A,
a, *b*, *c* show successive stages of reversal broadening. In
Fig. 1B the further stages leading to reversal doubling are
illustrated.
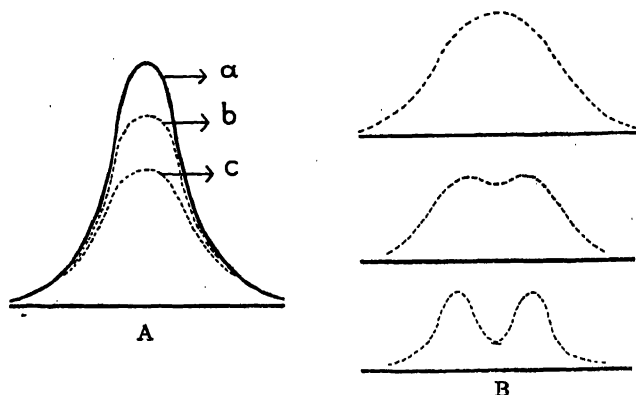
FIG. 1.—A. Shows how a line is broadened by self-absorption.
          B. Shows how further self-absorption produces reversal.

Development of special sources

To combat the effects of line broadening special sources
have been developed. The main essentials are that bril-
liance is required, yet the temperature, pressure and field
strength must be kept low. A brief resumé of the more
useful sources is as follows.

  1. *Hollow cathode discharge*
     This is a glow discharge maintained at a pressure of
     about a millimetre in a rare gas. A direct current

supply is used and the cathode, a hollow cylinder, is usually cooled, often with liquid air. Pressure, Stark and temperature broadening effects are all small and the brilliance is high.

2. *Low pressure arc*
   These have limited application but are of some use.

3. *Cooled low pressure Geissler discharge*
   A good deal can be done with such sources when carefully designed.

4. *High frequency electrodeless discharge*
   A high frequency discharge can be obtained by means of a thermionic valve oscillating on moderately short wavelengths (say 20 m.). The merit of this discharge is that it is quite bright at fairly low pressures and only small electric fields are involved, the result being very sharp line emission.

5. *Atomic beam*
   If a jet of atoms, moving in a high vacuum is viewed at right angles to the direction of travel of the atoms, then the resolved component of velocity in the line of sight is so small that Doppler width is very greatly reduced. It is possible by this means to reduce Doppler width to that which would result if a source were cooled to the abnormally low temperature of only 6° Abs.
   With this source the highest resolving powers can be used and the structures measurable are very small.

High resolution instruments

Not only must the lines be sharp, but the instruments employed must have high resolution and dispersion. Interferometers must generally be employed and the apertures and light losses are such with these instruments that brilliance in emission becomes a necessity. When it is remembered too that some components within a hyperfine structure are often very weak and that long exposures are experimentally difficult to obtain, the importance of source brightness is further emphasised.

The most important instrument in use is the variable gap Fabry-Perot interferometer, silvered for the visible and infra-red and aluminised for the ultra-violet. The compound Fabry-Perot (two different etalons in tandem) has found useful application also.

The quartz Lummer plate has contributed a good deal, particularly in the ultra-violet region. Echelons, both reflection and transmission, have been employed, but the application of all three instruments (the Fabry-Perot excluded) is restricted by the fixed dispersion. For the coarser structures, the higher orders of gratings have been utilised.

MULTIPLICITY IN LINE SPECTRA

IN order to be able to understand the origin of the hyper-fine structures of spectra, it is necessary to have a clear understanding as to how gross structure multiplets arise. It is not possible to give a comprehensive account here, and for a full treatment the reader is referred elsewhere.[1] The more important general features, in so far as they bear upon the subject of hyperfine structures, will, however, be discussed here. It will be assumed that the reader is familiar with the elementary Bohr theory of the hydrogen atom, and also understands how the Periodic Table has been built up by the process of completion of the electron shells. An excellent introductory account is given in Johnson's " Spectra " in this series.[2] The simplest type of spectrum, namely that arising from a hydrogen-like atom such as sodium, will first be discussed. Such an atom possesses only one valence electron, the transition movements of which give rise to the optical spectrum. The discussion will then be extended to two electron and later to more complex cases by the help of a vector model. Although the wave mechanics has shown that the vector model is not quite exact, yet it is extremely helpful and valuable as an aid to the solution of problems and sufficiently correct for our purposes.

One-electron spectra

A convenient example of a hydrogen-like atom is sodium, which consists of a nucleus and eleven outer electrons. In this atom, two inner electron shells, namely the K and L shells are completely filled, and in the third shell there is one electron, the valence or optical electron. For spectro-scopic purposes the first shell is denoted by the number 1, the second by 2, etc. In the vector model of the atom,

each electron is considered to be spinning, the mechanical moment of the spin being the same for each electron and equal to $\mathbf{s} . \dfrac{h}{2\pi}$, where $\mathbf{s} = \frac{1}{2}$ and h is Planck's constant.[3] $\mathbf{s}$ is called the spin quantum number of the electron. Since, in addition, an electron rotates in its orbit, it also possesses an orbital angular momentum, and the value of this orbital momentum is $1 . \dfrac{h}{2\pi}$ for each electron, where 1 is called the orbital quantum number. In contradistinction to the spin, different electrons may possess different 1 values ; they may have any of the values o, 1, 2, 3, 4, etc., according to the eccentricity of the orbit in which the electron moves.

<div align="center">TABLE I</div>

1 value . . .	o, 1, 2, 3, 4, . . .
Electron designation .	s, p, d, f, g, . . .
Atomic state . .	S, P, D, F, G, . . .

In general an electron moves in an elliptical and not in circular path around the nucleus, and orbits of the same major axis, but of different eccentricities, are possible for a given electron. *The numerical value of 1 is a measure of the ellipticity of the orbit*, the smaller the 1 value, the more eccentric is the path. An orbit of given eccentricity is designated by a letter, the letters corresponding to different 1 values. The particular letters which are employed are so used because of historical associations. Rows one and two of Table I show the electron designations for various 1 values.

It will be recalled that the first orbit is termed a 1 orbit, the second a 2 orbit, etc., and an electron in any orbit may have different 1 values. Thus an electron in the first orbit with $1 = $ o is called a 1s electron and similarly, for example, an electron in the second orbit with $1 = $ 1 is designated as a 2p electron. Using this notation the com-

plete structure of the *normal* sodium atom, which possesses eleven electrons, is written as $1s^2$, $2s^2$, $2p^6$, $3s$, meaning that there are two $1s$ electrons, two $2s$, six $2p$ and one $3s$ electron in the whole atom. The number of similar or "*equivalent*" electrons, as they are called, is indicated by the index. The optical spectrum is produced by movements of the $3s$ electron, for the inner shells, the first with two and the second with eight electrons, are completely filled, and only contribute to the spectrum in so far as they screen off the nuclear charge from the valence, or optical electron, as it is called.

Spectral terms of a one-electron atom

By "one-electron atom" is meant an atom with one valence electron, such as sodium or caesium. In such an atom only this one valence electron comes into consideration spectroscopically. The electron possesses both a spin and an orbital motion, and being a charged particle, these two angular momenta produce magnetic fields. The spin magnetic field and the orbital magnetic field interact with each other so that in effect the mechanical spin **s** * and the mechanical orbital moment **l** combine together to form a resultant by virtue of their magnetic fields. This resultant, called the inner quantum number, is denoted by the letter **j** and is obtained by the vectorial addition of **l** and **s**, that is **j** = **l** + **s**. Since **s** is constant and equal to $\frac{1}{2}$, and as **l** varies for different types of orbit, it follows that the inner quantum number also varies for orbits of different eccentricities. The sodium atom in the normal unexcited state has the optical electron in the $3s$ orbit and as seen from Table I the **l** value for an s orbit is zero, so that **j** = $\frac{1}{2}$ + 0, i.e. **j** = $\frac{1}{2}$. The same is true for $4s$, $5s$, $6s$, etc., orbits.

Term notation

So far only the notation for the optical electron itself has been considered, and a further symbol is required to

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* It is usual to omit the $\frac{h}{2\pi}$ factor since this is always understood. The letters **l**, **s**, **j** represent vectors, and are printed in heavy type.

describe the energy of the whole atom when the optical elec-
tron is in a given orbit. When this electron has a given l
value the atom itself is said to be in a given state, corre-
sponding to the notation given in the third row of Table I,
and it is seen that in the case of a one-electron atom, the
letter designating the state is the same as that describing
the electron, except that capital letters are used for atomic
states and small letters for electron orbits. An atomic
state is virtually a description of the energy and position of
the optical electron, and the different states, or different
energy values, which make up all the energy levels out of
which the spectrum arises, are called terms. To make this
clearer, it will be seen that, for example, a number of S
states are possible for $3s$, $4s$, $5s$, etc., electrons, and each of
these is called an S term.

In describing a term, the j value is written to the right.
For example, in the term arising from a $3s$ electron, since
$j = \frac{1}{2}$ a $^2S_{1/2}$ term is formed. The left-hand upper sub-
script is called the term multiplicity, and indicates the
maximum number of values j can have. For it will be
remembered that j is the resultant of the vectorial com-
bination of l and s, and in general a number of resultants
are possible. If l is greater than zero, j cannot have more
than $2s + 1$ values. This can be seen as follows. Since
s adds vectorially to l the values of j vary between $l + s$
and $l - s$, each value diminishing by one, i.e.

$$(l - s), \quad (l - s + 1) \ldots (l - 1), \quad (l),$$
$$(l + 1) \ldots (l + s - 1), \quad (l + s).$$

There are therefore $2s + 1$ values, so that the term multi-
plicity is given by $2s + 1$. In the case considered above,
as $s = \frac{1}{2}$ the multiplicity is two, and the term is called a
doublet term. In more complex atoms s can have other
values, and when $s = \frac{1}{2}$, 1, $\frac{3}{2}$, 2, etc., the terms are called
doublet, triplet, quartet, quintet, etc., the multiplicity
subscripts being 2, 3, 4, 5, respectively.

Consider what happens when the sodium atom is excited
so that the optical electron is forced out of its normal $3s$
orbit into the higher $3p$ orbit. Since the electron is now

in a p orbit, the l value is 1 (see Table I) and the atom is in a P state. Two values for j are now possible, that in which the electron spin s is parallel with l and that in which it is anti-parallel. There are thus two values of j namely, $j = l \pm s$, i.e. $j = 1 \pm \frac{1}{2}$, so that j may be equal to $\frac{1}{2}$ or $\frac{3}{2}$. It follows that two terms are formed, these being $^2P_{1/2}$ and $^2P_{3/2}$. The terms are doublet terms, as $s = \frac{1}{2}$ for the single electron concerned, and, as just shown, multiplicity is $2s + 1$. It is easy to see that a $3d$ electron (with $l = 2$) will produce $^2D_{3/2}$ and $^2D_{5/2}$ terms in a similar manner. Since, say, a $^2P_{1/2}$ term may be produced by either a $3p$, $4p$, $5p$, etc., electron, it is customary to specify the terms more completely by writing the designation of the optical electron before the term. For instance, the $^2P_{1/2}$ terms produced by $3p$ and $4p$ electrons respectively, are described as $3p \cdot {}^2P_{1/2}$ and $4p \cdot {}^2P_{1/2}$. Other examples are, say, $4d \cdot {}^2D_{3/2}$ and $5f \cdot {}^2F_{7/2}$, etc. A line transition from a $4p$ to a $3s$ orbit would be written as $3s \cdot {}^2S_{1/2} — 4p \cdot {}^2P_{3/2}$ as a particular instance.

Terms in alkali spectra

The terms which arise in alkali spectra are shown in Fig. 2. All the terms other than S terms are double, since two values for j are permitted, whereas for the S terms $J = \frac{1}{2}$.

In the two components of a doublet term, e.g. $4p \cdot {}^2P_{1/2}$ and $4p \cdot {}^2P_{3/2}$ that with the smaller j usually lies deepest, and *such a spectrum is called a normal spectrum.* In some atoms the terms are completely inverted, the biggest j value lying deepest and there exist regular intermediate stage graduations between normal and inverted spectra.

A group of terms such as $3p \cdot {}^2P_{1/2}$, $4p \cdot {}^2P_{1/2}$, $5p \cdot {}^2P_{1/2}$, etc., is called a sequence of terms, and each sequence tends to a common limit which represents the ionisation limit of the atom. When the optical electron is lifted to this limit it does not fall back, but leaves the atom, which is then charged, and is called an ion. The number 3, 4, 5, 6, etc., before the p in the term designation is called the current total quantum number n, and Fig. 2 shows that the intervals

between the components of a doublet term steadily diminish as n increases.

When the electron is excited and lifted up to a high orbit, it tends to fall back to a lower orbit. Not all transitions are possible, and amongst those which do occur some are more probable than others. Transitions are limited by a selection principle which states that l must change by $\pm$ 1
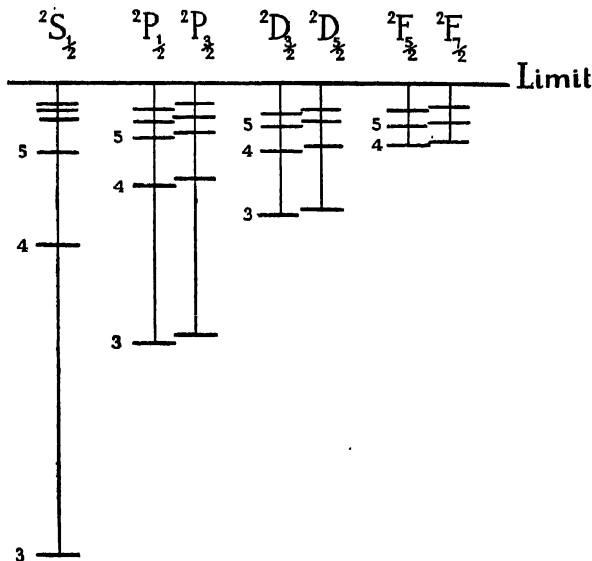
FIG. 2.—The term scheme of sodium and the alkali-like atoms.

and j by $\pm$ 1 or 0, the transition $\Delta j = 0 \rightarrow 0$ being excluded. Under special conditions of excitation these rules may be violated, but such departures need not concern us at present.

As $\Delta l = \pm$ 1, transitions from S to P or P to D (or vice versa) are allowed, but an S to D transition is, for example, forbidden. All the transitions, from, say, a given ^{2}P to a given ^{2}D state, that are allowed by the j selection

principle, together form a *multiplet*, and the multiplet is named according to the multiplicity of the terms involved, i.e. in this case it is called a doublet multiplet. A typical doublet multiplet is illustrated in Fig. 3, which shows how
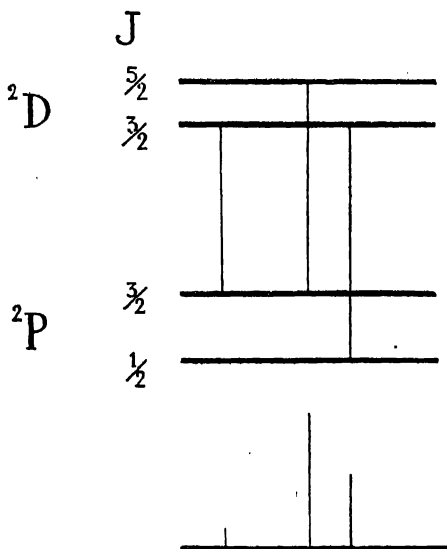
FIG. 3.—A typical doublet multiplet; note that three lines are produced but the doublet name is derived from the term multiplicity.

a ^2P—^2D multiplet arises. Some transitions are more probable than others, resulting in lines of differing intensity, and in the illustration the heights of the lines are drawn proportional to the line intensities. The intensities of the components of a multiplet obey laws which are very similar to those obeyed by hyperfine structures, and since the latter have to be considered in detail, it will be sufficient to state the "sum rule" which governs the relative intensities of the components of a given multiplet. Simply stated, the rule is that the sum of the intensities of all the lines coming

to any given j level is proportional to $2j + 1$. It is to be noted that a doublet multiplet can consist of more than two lines ; the doublet appellation refers to the *multiplicity* of the terms and not to the *number* of lines in the multiplet patterns.

Two-electron spectra : Electron couplings

Having examined the alkali-like spectra, the next step is to discuss the spectra produced by atoms which have two valence electrons, e.g. Ca or Hg, etc. The two valence electrons interact with each other, and as the principles employed here are fundamentally the same as those for more complex electron systems, they will be discussed in detail. As in the previous case considered, each of the two valence electrons possesses a spin angular momentum $s = \frac{1}{2}$, and an orbital angular momentum l which may have any of the values $0, 1, 2, 3, 4, 5$, etc. There are four vectors to take into consideration, and these may combine in different ways to form a resultant J which will represent the total angular momentum of the atom. (*In the vector notation small letters are used to represent specific angular momenta for individual electrons, and capital letters for resultant sums.*) The vectors may combine in a variety of ways and one may distinguish two extreme types of coupling called LS * and jj respectively.

LS coupling

There are four vectors which will couple in a two-electron atom, namely, s_1 and s_2, the two electron spins, and l_1 and l_2, the two orbital angular momenta. In LS coupling, the binding between the spins s_1 and s_2 is so strong that these form a resultant spin S. Correspondingly, the binding between the two orbital angular momenta l_1 and l_2 is strong and these add up to form a resultant orbital angular momentum L. This means that the linkage of the mutual spins is so strong that it is not influenced by the orbital

* This type is often termed Russel-Saunders coupling, after its discoverers.

angular momenta; at the same time, the linkage of the orbital angular momenta is such that the electron spins cannot affect it. There are now two resultant vectors S and L and these in turn couple to form a resultant J. As in the simple alkali case, the multiplicity is now $2S + 1$.*
Furthermore the term type is determined by the numerical value of the resultant L, i.e. for $L = 0, 1, 2, 3, 4, 5$, etc., the terms are S, P, D, F, G, H, etc. *It is important to notice that the term letter notation is not the same in capitals as the letter notation of the optical electron in small letters*, as was the case with hydrogen-like spectra. The selection rules now become

$$\Delta J = \pm 1 \text{ or } 0 [0 \rightarrow 0 \text{ excluded}]$$
$$\Delta L = \pm 1.$$

jj coupling

Whereas in LS coupling all the spins unite to form a resultant spin S, and all the orbital momenta form a resultant L, the case called jj coupling is different. The same four vectors s_1, s_2, l_1, l_2 are under consideration, but the mode of combination is altered. Here the coupling between the s_1 and l_1 of the one electron is so strong that it forms a resultant j_1. Similarly the spin and orbital momenta s_2, l_2 of the other valence electron form a resultant j_2. The other possible influences are not sufficient to break these pairings so that the two resultants j_1 and j_2 now couple to form a resultant J. Summarising then, in LS coupling all the l values form a resultant L and the s values a resultant S which then combine to form J, whilst in jj coupling the l and s of each electron combine to a resultant j for each electron, and then the j values add up to form J.

Regular intermediate stages exist between LS and jj couplings and these are conveniently shown below.†

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* s has always the value $\frac{1}{2}$, but S, being a resultant, may have other and larger values.

† See Pauling and Goudsmit, " Structure of Line Spectra " (1931).

$$\{(l_1l_2)(s_1s_2)\} = \{LS\} = J \ . \qquad . \qquad . \quad (1)$$
$$\{(s_1l_1)(s_2l_2)\} = \{j_1j_2\} = J \ . \qquad . \qquad . \quad (2)$$
$$[\{(s_1l_1)s_2\}l_2] = \{(j_1s_2)l_2\} = J \qquad . \qquad . \quad (3)$$
$$[\{(s_1l_1)l_2\}s_2] = \{(j_1l_2)s_2\} = J \qquad . \qquad . \quad (4)$$

Two vectors within a bracket are directly coupled together. The first and second cases are the LS and jj types already mentioned.

In the third case s_1l_1 give a resultant j_1 which breaks up the link between s_2l_2 and first combines with s_2. The vector pair j_1s_2 then combines with l_2 to give J. The fourth case is similar, except that j_1 first binds itself with l_2 instead of s_2.

It can be shown that no matter what manner of coupling may exist, the *number* and *type* of the terms which are produced by the vector combinations remain the same; this has considerably simplified analysis. The multiplicity has been defined as $2S + 1$, but since it is only in pure LS coupling that a resultant S exists, the multiplicity for jj or intermediate stage coupling has, in this sense, no real meaning. As, however, the number and type of terms are independent of the nature of the coupling, it is convenient to use the same notation, for the multiplicity gives the number of terms, independent of the existence of S. The greater number of actual spectra hitherto analysed are cases of the LS type of coupling, which will be illustrated by an example.

Graphical representation of coupling processes

As a typical example of a two-electron spectrum of the normal type, calcium will be considered. In the normal state calcium has two valence electrons, both of which are in $4s$ orbits and either of these may be excited, either separately or simultaneously. Let us first consider the case when only one of the valence electrons is excited, the other remaining permanently in its $4s$ orbit. The optical electron may go either into a ns, np, nd, etc., orbit according to the excitation energy given to it, and the two electrons with their different energies interact to give a resultant J.

In calcium, the coupling is LS in type, meaning that the electron spins unite to a resultant S and the orbital momenta to a resultant L. Two distinct classes of terms arise, those in which the two electron spins s_1 and s_2 oppose, giving a resultant $S = 0$, and those in which s_1 and s_2 add to form a resultant $S = 1$. The first group is a singlet group, the second a triplet (multiplicity $= 2S + 1$). The optical electron may have varying L values so that a set of singlet and a set of triplet terms arise.

The *singlet* set of terms is quite simply formed. The normal state of the atom is that in which both electrons are in $4s$ orbits, and therefore each has $l_1 = l_2 = 0$. In the singlet system $S = 0$ and as the resultant L also equals zero, then $J = L + S = 0$ so that the deepest term of the spectrum, i.e. the *normal* term, is $^1S_0$ or, more accurately described, $4s^2 \cdot {}^1S_0$. When an optical electron moves to $5s$, $6s$, etc., the terms formed are $4s \cdot 5s \cdot {}^1S_0$, $4s \cdot 6s \cdot {}^1S_0$, etc., so that a sequence of $^1S_0$ terms is produced. Instead of going into an s orbit, the optical electron may be lifted into a p orbit, for which $L = 1$. As before, the resultant S still equals zero, but the resultant orbital momentum L is equal to $l_1 + l_2 = 1$. The term therefore is a ^1P term and as $J = L + S$ it is a $^1P_1$ term. Similarly when the optical electron is lifted to a d orbit, a $^1D_2$ term is formed, etc.

In order to see how *triplet* terms arise, a vectorial graphical representation proves useful. The triplet system is that in which the two electron spins s_1 and s_2 act parallel so as to produce a resultant $S = 1$. Owing to the Pauli exclusion principle, it is impossible to have two electrons in $4s$ orbits with their spins parallel, for the Pauli principle states that no two electrons can exist together in the same atom if their n, l, j and m values are the same (m is the magnetic quantum number which exists when the atom is in a magnetic field). This principle excludes the possibility of having two $4s$ electrons with their spins parallel. The first allowed state is that in which, as before, one electron remains permanently in the $4s$ orbit and the other goes to a $5s$ orbit. Since the spins are parallel, $S = s_1 + s_2 = 1$, but $L =$

$l_1 + l_2 = 0$ for both electrons are in s orbits.   Hence as
$J = L + S$ a $^3S_1$ term is formed.   The optical electron
being also capable of moving to higher s orbits, a whole
sequence of $^3S_1$ terms is similarly produced.

The graphical representation of Fig. 4 enables us to see

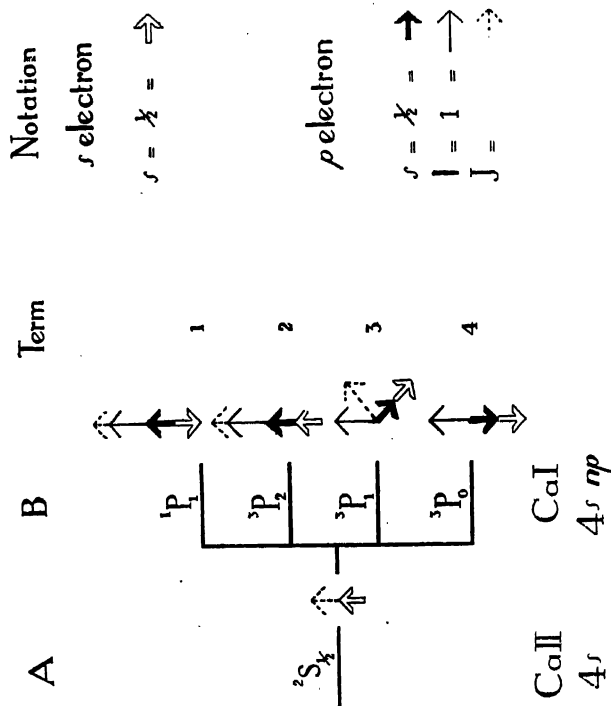FIG. 4.—The production of the ^1P and ^3P terms of Ca I.

what occurs when the electron is lifted into a p orbit.   As
before, the $4s$ electron has $l_1 = 0$ and $s_1 = \frac{1}{2}$, while the
p electron has $l_2 = 1$ and $s_2 = \frac{1}{2}$.   The two spins s_1 and
s_2 have formed a resultant $S = 1$, and similarly $l_1 + l_2 = 1$.
From this it is seen that J can have any of the three values

o, 1, 2, and the terms $^3P_0$, $^3P_1$, $^3P_2$ are produced. From the graphical point of view, it is very useful if we start from the $^2S_{1/2}$ ion term. That is to say, consider the atom ionised, in which state the optical electron is completely removed, leaving the other valence electron in the $4s$ orbit.

The ionised atom will now be in a state identical with the normal state of the one-electron type of atom, i.e. in a $^2S_{1/2}$ state. Now, to produce a Ca I atom with one electron in a p orbit all that is necessary is to add the vector representing the p electron to the vector representing the $^2S_{1/2}$ state of the Ca II atom. This is shown in Fig. 4. The left, A, shows the $^2S_{\frac{1}{2}}$ ionic term of Ca II in which the only existing vector is the electron spin, $s_1 = \frac{1}{2}$, of the $4s$ electron. This is shown vectorially by a thick hollow arrow in the vector picture at the right of the term. The direction of the resultant J is shown by means of a dotted arrow, and of necessity coincides with the direction of s_1 in the $^2S_{1/2}$ term. The effect of adding a $4p$ electron to the $4s$ electron is shown vectorially at B. The orbital angular momentum ($l_2 = 1$) of the $4p$ electron is shown by the long thin black arrow, and its spin ($s_2 = \frac{1}{2}$) by means of a short thick black arrow. [The reason for distinguishing between the spins of the $4s$ and $4p$ electrons, although both equal $\frac{1}{2}$, will appear later.] The four terms which result from the singlet and triplet combinations of $4s$ and $4p$ are shown at the right. The first term is the $^1P_1$ term previously discussed. In the second all the vectors act parallel, and so produce a $^3P_2$ term. The third term shows how both the spins couple to a resultant $S = 1$, which then combines at an angle with $L = 1$ to give a resultant $J = 1$. In the fourth the two spins still act parallel, but their resultant opposes L and a $^3P_0$ term is produced.

A schematic diagram of the more important terms in Ca I when one of the valence electrons remains in the $4s$ orbit and the other moves successively to s, p, d, f, g, etc., orbits is shown in Fig. 5. As in the hydrogen-like spectra, all these terms tend to a limit, which is the normal state in which the ion is left, in this case a $4s . ^2S_{1/2}$ state. *It is very convenient to imagine all the terms of an atom as being built up*

by the addition of an electron vector to the terms of the ion.
For example, the addition of a $5s$ electron to the $4s \cdot {}^2S_{1/2}$
state of Ca II produces the ${}^1S_0$ and ${}^3S_1$ terms of Ca I, and,
as shown graphically, a $4p$ electron produces ${}^1P_1$ and ${}^3P_0$,
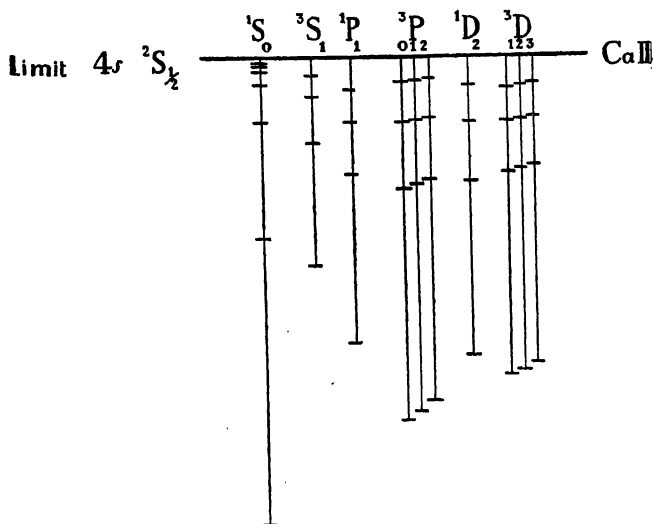
FIG. 5.—Part of the term scheme of Ca I built upon the $4s \cdot {}^2S_{\frac{1}{2}}$
series limit.

${}^3P_1$, ${}^3P_2$ terms.   The addition of d, f, g electrons can be
made in a similar way.

Series limits

It has so far been assumed that only one of the valence
electrons has moved into a higher orbit, but it is possible for
both to be displaced when excitation of the atom takes
place.   For example, the $3d$ orbit is higher than the $4s$ and
one electron may be lifted up into this orbit and remain
there, whilst the other may be lifted to an s, p, d, f, etc.,
orbit.   Or else the first electron is lifted to $4p$ and the second

to some other orbit. In each case the terms will tend to different limits, since the ion is left in a different state. Thus, in the first case previously discussed, where one electron was permanently in a $4s$ orbit, the calcium ion is left in a $4s$. $^2S_{1/2}$ state when the optical electron is completely removed. In the second case mentioned above, the electron of the ion is left in a $3d$ orbit when the optical electron is

FIG. 6.—The main terms and series limits in the spectrum of Ca I.

removed, so that the ion may be left either in a $3d$. $^2D_{3/2}$ or a $3d$. $^2D_{5/2}$ state. It follows that all the terms of the calcium atom, which arise when one electron remains in a $3d$ orbit and the other moves to other orbits, tend to two limits, $^2D_{3/2}$ and $^2D_{5/2}$. These two terms lie close together, being members of a doublet group, but are both far away from the $^2S_{1/2}$ state which was the single limit reached by all the terms when only one electron was excited. In an identical manner the terms produced when one electron is in the

$4p$ orbit and the other is in some other orbit tend to the limits $4p$. $^2P_{1/2}$ and $4p$. $^2P_{3/2}$, which again lie close together but are both far removed from the ^2D terms of the previous case. The limits reached by the terms of Ca I are shown in Fig. 6 and are seen to be widely separated.

In order to be able to build up term schemes correctly, it is necessary to know exactly what the series limits will be and to which particular limit a given sequence of terms will converge. It will be seen later that this has a very important bearing upon the problem of hyperfine structures, and for this reason series limits have been discussed here. Complete tables of series limits have been investigated by Hund [4] and the reader is referred to Hund's work for particular cases. Hund [5] has given two sets of limits, one set being those to which normal terms tend ; the other for inverted terms. An example of the application of the rules will be given later when series limits are applied to hyperfine structures.

Equivalent electrons

The Pauli exclusion principle strictly limits the number of electrons with the same n and l value in any atom. In a given orbit there cannot be more than a fixed number of, say, p or d of f electrons. Such electrons are called equivalent electrons. As an example of an atom which has many equivalent valence electrons, the bromine atom may be cited. In the normal state it has seven valence electrons, two of which are in $4s$ orbits and five in $4p$ orbits. The configuration is called a $4s^2$. $4p^5$ electron configuration, using the notation already described. The two $4s$ electrons are equivalent, and the five $4p$ electrons are also equivalent. The $4s^2$ group is called a closed group, and takes practically no part in producing the spectrum, so that for present purposes it may be neglected, and only the $4p^5$ group need be considered. The spectral terms of the atom are produced by one of these electrons moving into various orbits. In the normal state the five $4p$ electrons are arranged so that the resultant $S = \frac{1}{2}$ and the resultant $L = 1$. This means that ^2P terms are formed and these are the deepest lying

terms, the $^2P_{3/2}$ term being deeper as the multiplets are inverted. The remaining important terms of the spectrum are produced by the moving optical electron.

The first group of terms arises when one of the $4p$ electrons is lifted up to the $5s$ orbit, so that the configuration becomes $4s^2 . 4p^4 . 5s$. Another group is formed if the optical electron goes instead into a $5p$ orbit producing a $4s^2 . 4p^4 . 5p$ configuration, and so on. Each separate electron configuration forms a number of terms and these can all be conveniently built up by treating the $4s^2 . 4p^4$ electron group as a core to which the optical electron is added in the $5s$, $5p$, etc., orbits. It is seen that the process is not very different from that involved in building up the two-electron spectra, for in the latter two electrons were coupled together, and at present one electron is to be coupled to a core.

The series limits must be known before any attempt to build up the terms can be made. All the terms of the bromine atom can be predicted by means of Hund's theory. and the most important of these are shown in Table II.[6]

TABLE II

Basic Terms of the Ion Br. II.	^3P.		^1D.	^1S.
Electron Configuration. $4s^2 . 4p^5$ $4s^2 . 4p^4 . 5s$ $4s^2 . 4p^4 . 5p$ $4s^2 . 4p^4 . 4d$ etc.	^2P ^2P ^4P $^2(SPD)$ $^4(SPD)$ $^2(PDF)$ $^4(PDF)$		^2D $^2(PDF)$ $^2(SPDFG)$	^2S ^2P ^2D

In Table II the electron configurations are shown in the first column and each configuration produces the group of terms shown in the remaining columns. It is usual to distinguish between two classes of terms called odd and even terms. Odd terms are those in which the sum of the l values of the individual electrons of the term configuration

is odd and even terms those in which the sum is even.   For example, in the previously considered case of Ca a $4p^2$ term is even and a $4p \cdot 4d$ term is odd.   In Br I $4s^2 \cdot 4p^5$ terms
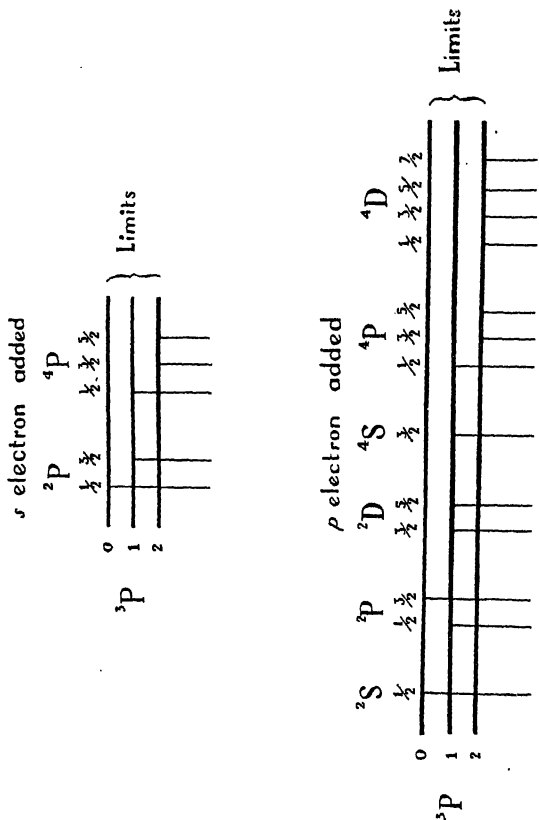

FIG. 7.—Series limits of important terms of the Br I spectrum.

are odd, $4s^2 \cdot 4p^4 \cdot 5s$ even, etc.   *Transitions may only take place between odd and even terms*.   These terms are sometimes distinguished by superscripts, but since the electron configurations are always given here, superscripts are un-

necessary. As Table II shows, transitions such as $\mathbf{P} \rightarrow \mathbf{P}$ or $\mathbf{P} \rightarrow \mathbf{F}$ are possible providing they are odd-even transitions. In addition to this L restriction, transitions can only take place when $\Delta \mathbf{J} = \pm 1$ or 0 ($0 \rightarrow 0$ excluded).

In Table II the basic ion terms of Br II are shown in small type. These are produced by the configuration of the ion Br II and are the basic terms which produce the terms of Br I when the optical electron is added. They are also the series limits, that is, the limits to which the Br I terms converge. In order to avoid making the table too cumbersome two abbreviations are used. First, a term written as $^3\mathbf{P}$ or $^4\mathbf{P}$ means the whole sequence of allowable J values, in these cases, $^3\mathbf{P}_0$, $^3\mathbf{P}_1$, $^3\mathbf{P}_2$ and $^4\mathbf{P}_{1/2}$, $^4\mathbf{P}_{3/2}$, $^4\mathbf{P}_{5/2}$ respectively. Second, a group of terms $^2\mathbf{S}$, $^2\mathbf{P}$ and $^2\mathbf{D}$ is written $^2(\mathbf{SPD})$ and similarly for other multiplicities. Each horizontal row shows the terms which arise from a given configuration, and the limits to which these terms tend is indicated by the column in which the terms are found.

The question of series limits is of importance, and since the limits for normal and inverted spectra are different, care must be taken to use the correct limits. The terms in Br I are inverted ; a pictorial diagram of the limits is given in Fig. 7. The terms of Br II are also inverted and this appears in the diagram. The diagram illustrates two cases only, namely the important $4s^2 \cdot 4p^4 \cdot 5s$ and $4s^2 \cdot 4p^4 \cdot 5p$ terms which tend to the $^3\mathbf{P}$ limit. The limiting $^3\mathbf{P}$ terms are shown by the thick horizontal lines and form an inverted multiplet (the drawings are schematic and not to scale) as shown by the J values on the left. The effect of adding the $5s$ electron is shown by the vertical lines which indicate to which limit each term sequence tends. For instance, $^2\mathbf{P}_{1/2}$ tends to the limit $^3\mathbf{P}_0$ whilst $^4\mathbf{P}_{1/2}$ tends to $^3\mathbf{P}_1$. Conversely the $^2\mathbf{P}_{1/2}$ term of Br I is formed when the $5s$ electron is added to the $^3\mathbf{P}_0$ term of Br II, and the $^4\mathbf{P}_{1/2}$ term of Br I is formed by adding the electron to the $^3\mathbf{P}_1$ term of Br II. The method by which this is obtained will be shown later by means of a vector diagram. The lower diagram shows the effect of adding a $5p$ electron to the ion terms, giving in fact the terms and limits of the $4s^2 \cdot 4p^4 \cdot 5p$

configuration.   For comparison purposes Fig. 8 shows how
the series limits for normal and inverted multiplets are
different, although similar multiplets are considered.
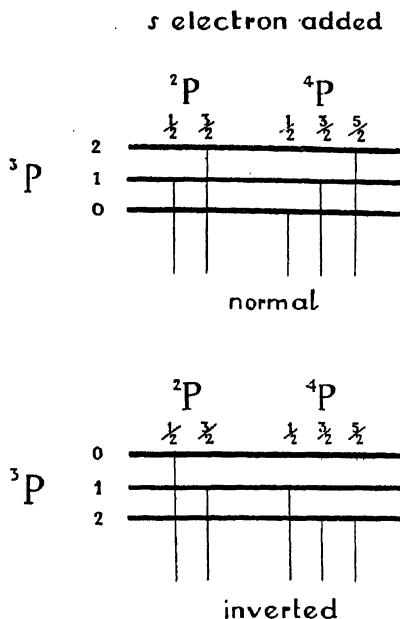
FIG. 8.—Showing the difference between the series limits in
normal and inverted spectra.

Vector coupling in bromine

The vector coupling in bromine is somewhat similar to
that of a two-electron spectrum and is shown for the
$4s^2 . 4p^4 . 5s$ configuration in Fig. 9.   In effect, the optical
electron $5s$ is to be coupled vectorially to the core $4s^2 . 4p^4$.
The core produces the $^3P_0$, $^3P_1$, $^3P_2$ inverted multiplet
terms shown at the left, which are the series limits, so that
the core is equivalent to a vector with $L = 1$ and $S = 1$,

for only such resultants will give a ³P multiplet.* The vector diagrams for the ³P basic ion terms of Br II are
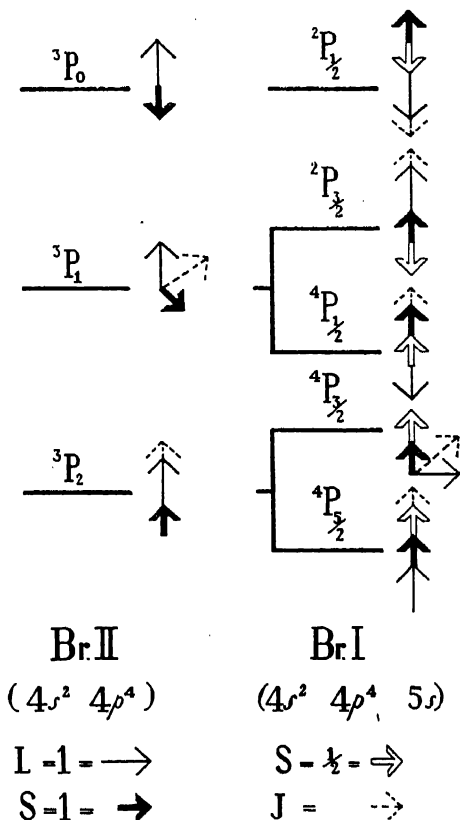
FIG. 9.—Vector coupling diagram showing how the ²P and ⁴P multiplet terms of the $4s^2 . 4p^4 . 5s$ configuration of Br I arise.

* In order to avoid complication it is assumed that strict LS coupling takes place. This is not true for bromine, but as it has only been chosen as an example because of its many valence electrons, the gloss is of no consequence here.

shown to the right of the terms. The long thin black arrow gives the resultant $L = 1$ and the short thick black arrow the resultant $S = 1$ (compare Fig. 4). As the terms are inverted, the largest J value (2) lies deepest. As before, the direction of J is shown by the dotted arrow.

The result of coupling the $5s$ electron to the core is shown at the right and this should be studied carefully. The electron is added in LS coupling which means that *the original coupling of the L and the S can be broken, but the individual* ll *couplings and* ss *couplings remain intact.* The new s value of the added electron may combine either parallel or anti-parallel with the already existing S value of the core, to form a new resultant S. The same is true for L (in this case the l of the added electron happens to be zero). The new L and S values then combine in the usual manner to give J. The $5s$ electron is shown by means of a short thick hollow arrow and *is always added in the same direction (either positively or negatively) as the original S value of the core.*

In the two higher lying Br I terms, the spins oppose, the resultant spin quantum number is $\frac{1}{2}$, producing an inverted ²P doublet. In the three deeper terms the resultant spin of the core acts parallel to that of the $5s$ electron, so that the terms are ⁴P ($S = \frac{3}{2}$ and multiplicity $= 2S + 1$) and are also inverted.

The vector method just described can be used for all configurations if the terms predicted by Hund's theory are taken as a guide and the correct series limits used.

Interval rule

In most of the diagrams previously given, the number and description of the terms of a multiplet has been given, but little attention has been paid to the relative positions of the terms such, for example, as the relative spacings between the terms of ³P group. In a normal triplet, the terms lie in the order ³P₀, ³P₁, ³P₂, the term with the smallest J value lying deepest. The interval between the first pair of terms is different from that of the second

pair, because the interaction energy between the spins and angular orbital momenta differs for the various terms, and the position of a term depends upon this interaction energy. It can be shown that, in **LS** coupling, the interaction energy between the resultant spin **S** and the resultant angular orbital momentum **L** is given by **E**, where

$$\mathbf{E} = \mathbf{A}' \,.\, \mathbf{SL} \cos (\mathbf{SL}),$$

A′ being called the interval factor for a reason which will appear later. The interaction energy between two vectors is proportional to the cosine of the angle between those vectors, and it can be shown that the above expression is equivalent to

$$\mathbf{E} = \frac{\mathbf{A}'}{2} \,.\, \{\mathbf{J}(\mathbf{J} + 1) - \mathbf{L}(\mathbf{L} + 1) - \mathbf{S}(\mathbf{S} + 1)\}$$

This formula expresses what is known as the Landé Interval Rule, after its discoverer, and from it the ratio of the intervals in a multiplet can be calculated.

Since the position of a term is given by its interaction energy, the difference of energy between two terms will be proportional to their separations and the formula shows that for a multiplet group arising from a given **S** and **L**, the energy differences of the different terms are proportional to the differences of the $\mathbf{J}(\mathbf{J} + 1)$ values. With a ⁴D multiplet group, for example, $\mathbf{S} = \frac{3}{2}$ and $\mathbf{L} = 2$, giving four terms with the **J** values $\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$. According to the Landé rule the successive energy differences between adjacent pairs of terms, being proportional to $\mathbf{J}(\mathbf{J} + 1)$, are in the ratio

$$\{\tfrac{7}{2} \cdot \tfrac{9}{2} - \tfrac{5}{2} \cdot \tfrac{7}{2}\} : \{\tfrac{5}{2} \cdot \tfrac{7}{2} - \tfrac{3}{2} \cdot \tfrac{5}{2}\} : \{\tfrac{3}{2} \cdot \tfrac{5}{2} - \tfrac{1}{2} \cdot \tfrac{3}{2}\},$$

that is, in the ratio 7 : 5 : 3, or that the ratios of the *intervals* of the terms of the multiplet are the same. It will be seen that these ratios are given directly by the ratios of the different **J** values when the smallest **J** value is neglected. This simplified form of the Landé rule is true for all cases in which strict **LS** coupling takes place. It is both true for normal and for completely inverted multiplets, but it will be obvious that when a multiplet is partially inverted

3

the rule completely fails. Whilst the *ratio* of the intervals between the terms is a function of **J**, the actual separations depend upon the value of the interval factor **A′**. This is determined by the distance of the electrons from the nucleus, the degree of penetration of the orbits, the screening effect of other electrons, and the interaction energy between the
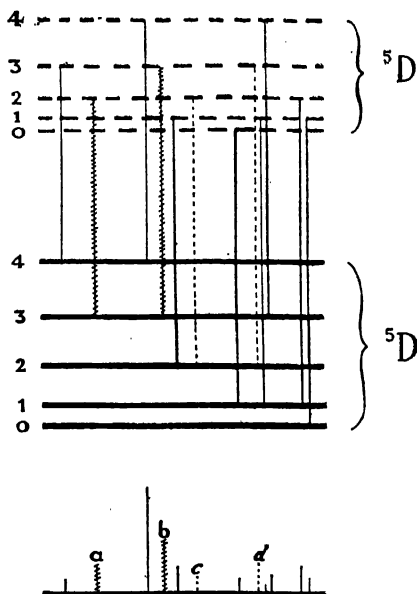
FIG. 10.—A typical $^5D - {}^5D$ multiplet pattern.

electrons themselves. The interval factor, therefore, differs for different multiplets, usually diminishing as the n of the optical electron increases. For this reason the separations in, say, the $4s \cdot 4p \cdot {}^3P$ multiplet of Ca I are greater than those in the $4s \cdot 5p \cdot {}^3P$ multiplet, although the ratios of the intervals are the same in both cases (in effect, the difference is merely one of scale).

An example of the line pattern formed by the transitions

between two multiplet terms is shown in Fig. 10, the case illustrated being that of transitions between two ^5D multiplet term groups. The interval factor of the upper set of terms is made less than that of the lower, but the interval rule is obeyed by both. The intensities of the lines differ according to the intensity rule on page 18. The resulting line pattern is complex because of the different interval factors and the varying intensities.

The line pattern of a multiplet

The line pattern of a multiplet can vary in width from a fraction of a wave number to several thousand wave numbers, and various methods have been used to assist in sorting out members of a multiplet from a large group of lines. *The most important way is the method of constant frequency differences* which can be seen from Fig. 10. An examination of the transitions shows that the two hatched lines *ab* have the same frequency difference as the two dotted lines *cd*, namely the interval between the upper terms with $J = 3$ and $J = 2$ respectively. It follows that a search among the lines suspected to belong to the multiplet will reveal this common difference, even when other foreign lines are present. It will be observed that a large number of common differences exist, and from these the multiplet can generally be built up, due regard being paid to the intensities which should obey the intensity law. There are, of course, many multiplets in which the intensity or interval rules break down and other means must be used to assist in analysis, such as Zeeman effect observations.

For further study in multiplet analysis the reader is referred to Hund's " Linienspektra ".

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THE EFFECT OF A NUCLEAR SPIN

Nuclear spin

Two types of hyperfine structure occur in line spectra, and these arise from entirely different causes. One type, called the isotope hyperfine structure, is due to the fact that many elements are not simple but consist of a number of isotopes. Since the separate isotopes of an element have identical extra-nuclear electron configurations, the spectra emitted by each of these are almost the same, and the lines of the one isotope practically coincide with the lines of the other. There is, however, in some cases, a measurable displacement for certain lines, the displacement being due either to the different masses or varying electrical properties of the different isotopic nuclei or else to the motion of the nucleus. In favourable cases these displacements can be observed as a hyperfine structure effect. This will be discussed in a later chapter.

The second type of structure arises because the nuclei of certain atoms have the property of a spin. It was first suggested by Pauli[1] that hyperfine structures (excluding isotopic effect) could be accounted for if it were assumed that the nucleus possessed a magnetic moment which perturbed the motions of the external electrons. This nuclear magnetic moment would couple vectorially with the magnetic moment of the valence electrons and behave as if a new quantum number had been introduced. If the nuclear and the electron magnetic moments couple in accordance with the usual vector rules, each electron term would be divided into a group of terms, the energies varying between the two limits formed when the nuclear moment is parallel and anti-parallel to the electron moment. In between these limiting terms further energy states may occur, the number depending on the quantum values of the

respective moments. The expression "*level*" will be retained to describe any of these hyperfine structure energy levels and the word "*term*" confined to denote the gross structure energy state.

Associated with the magnetic moment is a mechanical moment, which being quantised, becomes some multiple of $h/2\pi$. The mechanical moment is usually denoted by $I\dfrac{h}{2\pi}$ and the coefficient I is termed the nuclear spin. The existence of a nuclear spin had already been previously inferred, for the nuclei of certain atoms, from the study of band spectra. The investigation of the band spectrum of hydrogen showed definitely that each of the protons, which are the nuclei of the hydrogen atoms forming the hydrogen molecule, possesses a spin with $I = \frac{1}{2}$, i.e. the mechanical moment of the spinning proton is $\frac{1}{2}\dfrac{h}{2\pi}$, the same as in the case of the spinning electron. The ratio of the magnetic moment of the proton to that of the electron should be approximately in the inverse ratio of the two masses so that the magnetic moment of the proton should be about $\frac{1}{1840}$ that of the electron.* This explains the minuteness of the scale of hyperfine structures, in comparison with that of the ordinary gross structure multiplet. A study of the intensities of the band spectra of homogeneous molecules seems to point to the rule that the nuclear spin of light even atomic weight elements of mass a multiple of four is zero, while the odd elements have half integral spin values.[2] It can be shown that if the identical nuclei of the two atoms forming a homogeneous dipolar molecule have a nuclear spin I, the alternate lines in the rotational structure of the band spectrum have an intensity ratio $\dfrac{I+1}{I}$. When $I = 0$, the ratio becomes infinite, so that alternate lines are absent. This occurs in the spectra of He_2, C_2, O_2 and S_2.

* Actually it is 2·8 times greater than the value expected on the simple theory (p. 97).

Nuclear spins are usually found to be half integral and vary in value from $\frac{1}{2}$ to $\frac{9}{2}$. A detailed discussion will be given later of nuclear building-up processes with reference to the experimental values of the spins.

Interaction of nuclear and electron magnetic moments

As we have shown in the previous chapter the resultant moment of the electron system of an atom is given by **J**, so that if the atom possesses a nuclear spin **I** it is to be expected that the two vectors **I** and **J** should combine to form a resultant quantum number. This is termed the *hyperfine structure quantum number*, and is denoted by the letter **F**, which is a vector quantity, giving the total angular momentum of the whole atom. We find that **I** and **J** can combine vectorially to give a number of values so that each term of the spectrum (henceforth called the gross structure term) will divide into a tiny multiplet group of hyperfine structure terms, which for purposes of differentiation will be referred to as *levels*. The values that **F** can have are given by the vectorial relation $\mathbf{F} = \mathbf{I} + \mathbf{J}$, so that by analogy with the case of multiplets previously discussed it will be seen that if **J** is larger than **I** the total number of combinations possible is $2\mathbf{I} + 1$, hence the gross structure term divides into $2\mathbf{I} + 1$ levels. If, on the other hand, **J** is less than **I** the number of arrangements which is possible is $2\mathbf{J} + 1$. Since many terms split up in this manner, a gross structure line will have the line structure of a multiplet on a minute scale, and general considerations show that a selection principle will operate in the production of this hyperfine structure multiplet. The predicted and observed selection principle is $\Delta\mathbf{F} = \pm 1$ or o (o $\rightarrow$ o being excluded), and hitherto no exceptions to this rule have been found.

The interaction energy between the two vectors **I** and **J** is dependent upon a number of different factors. First, it depends upon the value of the magnetic moment of the nucleus as distinct from its mechanical moment, for it is primarily the magnetic fields which couple. It is, of course,

true that the magnetic fields arise because the charged particles in motion have mechanical moments, but since the coupling between the mechanical moments occurs through magnetic linkage, it is the value of the magnetic moment that determines the interaction energy of $\mathbf{I}$ and $\mathbf{J}$. The nuclear magnetic moment is usually written as μ, where $\mu = \mathbf{I} \cdot g(\mathbf{I})$, so that $g(\mathbf{I})$ is the ratio of the magnetic to the mechanical moment when quantum units are employed. $g(\mathbf{I})$ is a pure number, and as its value is determined by the internal structure of the nucleus, it may be very small at times. A second factor affecting the interaction energy is the nuclear charge, for the higher the degree of ionisation the greater is the coupling energy between the extra-nuclear electron moment $\mathbf{J}$ and the nuclear spin $\mathbf{I}$. A third factor which is extremely important depends upon the eccentricity of the orbit of the optical electron. If the orbit is very eccentric, a high degree of penetration of the inner shells takes place and the optical electron approaches closely to the nucleus so that the coupling becomes very strong. It will be apparent that the coupling energy of an s electron will generally be much greater than that of a p electron, etc.

Let us consider a one-electron system ; it is convenient to imagine the coupling between $\mathbf{I}$ and $\mathbf{J}$ as consisting of two parts. $\mathbf{I}$ couples with the orbital angular moment of the electron, that is, $\mathbf{IL}$ coupling takes place, and $\mathbf{I}$ couples with the electron spin so that $\mathbf{IS}$ coupling also occurs. When these two effects are added the interaction energy between nucleus and electron is obtained.[3] The final result shows that the energy $\mathbf{W}$ is given by the expression [4]

$$\mathbf{W} = \mathbf{A} \cdot \mathbf{IJ} \cdot \cos(\mathbf{IJ})$$

which can be reduced to the form

$$\mathbf{W} = \frac{\mathbf{A}}{2}\{\mathbf{F}(\mathbf{F} + 1) - \mathbf{J}(\mathbf{J} + 1) - \mathbf{I}(\mathbf{I} + 1)\}.$$

Comparing this with the formula previously given for ordinary multiplets it will be seen that the two formulæ are identical if $\mathbf{J}$, $\mathbf{L}$ and $\mathbf{S}$ are replaced by $\mathbf{F}$, $\mathbf{J}$ and $\mathbf{I}$. Since this is identical in form to the Landé formula for gross structure multiplets, the energies of the hyperfine structure

levels are also such that they will obey the Landé interval rule. The interval factor of the hyperfine structure multiplet A can be approximately calculated for the simple case of one electron spectra. It is found that A is proportional to

$$g(I) \cdot \frac{Z_i z^2}{n^3 L(L + \frac{1}{2})(L + I)},$$

where Z_i and z are respectively the effective electric charges of the nucleus in the inner and outer portions of a partially penetrating orbit, and n is the effective Rydberg quantum number. This formula includes the conditions previously referred to concerning the value of the nuclear magnetic moment, the nuclear charge and the degree of electron penetration. Calculation shows that the interval factor for the gross structure multiplet, A' of a one-electron system differs from the above value A by the factor $g(I)/Z_i$. From this it follows that the ratios of the scales of hyperfine structures to gross structure multiplets should be given approximately by $g(I)/Z_i$, but the formula is only very approximately correct, and the agreement with experimental results is only partial.

The formulæ for the hyperfine structure interval factors have only been developed for a few electron systems, but although the general theory is very incomplete, a number of important facts have already been deduced and experimentally verified. As previously stated the width of a structure in a term, that is to say, the total spread of the hyperfine structure multiplets, depends upon the coupling between I and J. This, in turn, depends upon the closeness of approach of the optical electron to the nucleus. The more elliptic the orbit, the more likely will the electron penetrate the inner shells. It will not only approach the nucleus more closely, but, when it penetrates closed electron shells, the screening effect of these shells will be reduced. This is equivalent to a considerable increase in the effective nuclear charge which further increases the tightness of the coupling, as it is called. Since the smaller the l value of an orbit, the more eccentric is its shape, it will be expected that electrons in s orbits will produce

much wider structure than electrons in p orbits. Correspondingly, the width of a $4s$ electron term should be greater than that of a $5s$ electron. Special attention may be directed to the case of p orbits. There are two distinct kinds, depending upon whether the electron spin assists or opposes the orbital angular momentum. In particular, in $\mathbf{jj}$ coupling the p electron can have $\mathbf{j}$ values $\frac{1}{2}$ or $\frac{3}{2}$ [for $\mathbf{l} = 1$ and $\mathbf{s} = \frac{1}{2}$]. These different orbits are designated as $p_{1/2}$ and $p_{3/2}$ respectively. The $p_{1/2}$ electron is in the more elliptical and more penetrating orbit and should produce wider fine structures than the $p_{3/2}$ electron. This has been verified experimentally.

Hyperfine structure in one-electron spectra

The vector model previously employed to illustrate gross structure multiplets can also be applied to study hyperfine structure multiplets.

The first new consideration is the question of the numerical value of the nuclear spin which introduces a complication. For example, two atoms may give spectra in which the gross structure multiplets are identical, except that their scales differ, but if the atoms have different nuclear spins, the hyperfine structures of the two spectra will be totally different. This can be made clear by specifying a certain value for I and it will then be shown how a variation in I will affect the levels of the terms.

As an example of the types of structures which are to be expected in one-electron spectra, a case like that of sodium will be considered. Referring to Fig. 2 we see that the deepest lying term in sodium involves the most penetrating electron and is the $3s$. $^2S_{1/2}$ term. Next to it come the two terms $4p$. $^2P_{1/2}$ and $4p$. $^2P_{3/2}$ which involve p electrons. We will examine the structures of the two lines $3s$. $^2S_{1/2}$—$4p$. $^2P_{1/2}$ and $3s$. $^2S_{1/2}$—$4p$. $^2P_{3/2}$. These two lines are the well-known yellow D lines of sodium. For simplicity we shall assume the nuclear spin I of sodium to be equal to $\frac{1}{2}$. This spin is to be coupled with each of the three terms concerned in producing the lines, in order to see what hyperfine structure levels will arise. The $3s$. $^2S_{\frac{1}{2}}$ term has the

J value $\frac{1}{2}$ and as the spin I is $\frac{1}{2}$, it is obvious that I and **J** can only combine in two ways, to give $F = o$ or $F = 1$ (it will be remembered that the maximum number of levels is $2J + 1$ or $2I + 1$ according to whether J or I is the smaller). The F value o is produced when the nuclear spin and the electron spin oppose each other, and the F value 1 arises
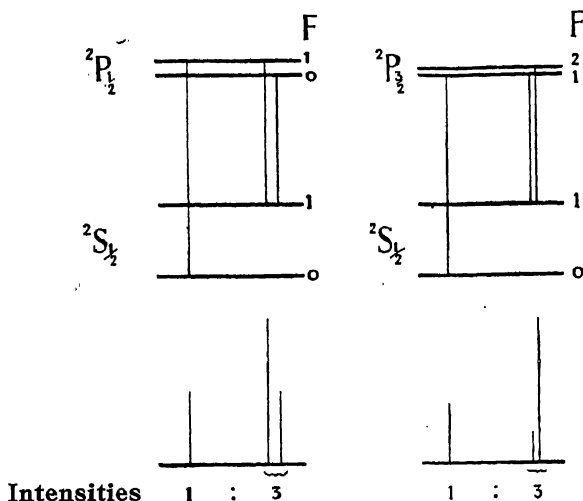

Intensities   1   :   3   1   :   3

FIG. 11.—Hypothetical structures of the sodium D lines, assuming
    that the nuclear spin is $\frac{1}{2}$.   Because of instrumental difficulties
    in resolving power and natural line widths, both the D lines
    have the same apparent structure, namely doublets in which
    the intensity ratio is 3 : 1.

when the two spins act parallel.*   It follows therefore that the $3s \cdot {}^2S_{1/2}$ term is double.

In this particular case $I = \frac{1}{2}$ and as all the J values in sodium are $\gg \frac{1}{2}$ every term of the spectrum must also be double.   The $4p \cdot {}^2P_{1/2}$ term will have the two F values o and 1 as in the previous case, but in the $4p \cdot {}^2P_{3/2}$ term

* The question as to true spin direction of an electron and of a
spinning nucleus is somewhat modified by the wave mechanics,
but for simplicity the vector model is adhered to here.

the F values will be 1 and 2, for J equals $\frac{3}{2}$ and I equals $\frac{1}{2}$, hence F = 1 or 2. Since both the lower and upper term of each of the two lines are double, each line will be a tiny multiplet. The structure of the common lower $3s \, . \, {}^2S_{1/2}$ term will be much wider than that of the upper terms, since an s electron is here involved. The structure of $4p \, . \, {}^2P_{1/2}$ will be somewhat greater than that of $4p \, . \, {}^2P_{3/2}$. Remembering the selection principle, $\Delta F = \pm 1$ or 0 (0 $\rightarrow$ 0 excluded) it is seen from Fig. 11 that each of the D lines will have three components. If the structures in the p terms are very small, and in sodium this is the case, the separations of the upper terms cannot be easily experimentally resolved and both lines appear to have the same structure, namely two components, the intensity ratio and frequency separation being the same for both of the D lines. It has been shown by Fermi [5] that in the s terms of one-electron spectra, the nuclear spin can be calculated from the intensity ratio of these apparent doublets, when the upper terms are unresolved. It can be shown that the quantum weight of a hyperfine structure level is 2F + 1. By this is meant that the sum of the intensities of all the lines coming to a level of given F value is proportional to 2F + 1. If I is the nuclear spin, the F values of the two levels of the ${}^2S_{1/2}$ term are $I + \frac{1}{2}$ and $I - \frac{1}{2}$ respectively. The intensity ratio of the two components of the doublet is therefore

$$\frac{2(I + \frac{1}{2}) + 1}{2(I - \frac{1}{2}) + 1} = \frac{I + 1}{I},$$

so that the accurate measurement of the intensity ratio will give the spin, I. Experimentally this is very difficult to determine, because the lines involved are resonance lines, which usually suffer self-absorption and this gives rise to false intensity measurements. In the case under consideration, the intensity ratio of the components in both the D lines would be 3 : 1. It is easy to see by making I equal to zero, that the formula given above is self-consistent. The intensity ratio in the hyperfine structure doublet then becomes 1 : 0, meaning that one line is missing. In other

words, the doublet becomes a single line when the atom has no nuclear spin, which is what one expects. Measurements have been carried out upon intensity ratios of doublets of alkali resonance lines,[6] but the results are usually disturbed by reversal.

Effect of varying nuclear spins

The calculated structure of the D lines becomes very different for different values of I, although the observed

Intensities   5 : 7   5 : 7
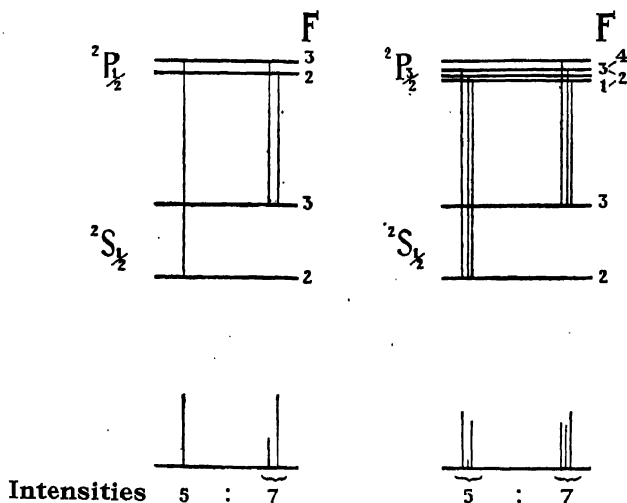
FIG. 12.—Hypothetical hyperfine structure of sodium D lines with the assumed nuclear spin of $\frac{3}{2}$. Two doublets are formed, the separation being 0·06 cm.$^{-1}$, and the intensity ratio 5 : 7.

structure may not appreciably change. The latter effect is, however, only accidental and is due to the fact that the structure in the *s* electron term is so much wider than in that of the *p* electron. The pattern formed by a larger spin such as $\frac{5}{2}$ is shown in Fig. 12. The $3s \cdot {}^2S_{1/2}$ term again divides into two levels, but as $J = \frac{1}{2}$ and $I = \frac{5}{2}$

the F values now become 2 and 3 respectively. The $4p$. $^2P_{1/2}$ term behaves in the same manner, except that the structure is on a smaller scale. As a result $3s$. $^2S_{1/2}$—$4p$. $^2P_{1/2}$ has three components, two of which are grouped closely together.

With a nuclear spin of $\frac{5}{2}$ the $4p$. $^2P_{3/2}$ term is no longer

F

4

3

$J = \frac{3}{2} = \text{---}\!\!\rightarrow$

2

$I = \frac{5}{2} = \text{····}\!\!\rightarrow$

1
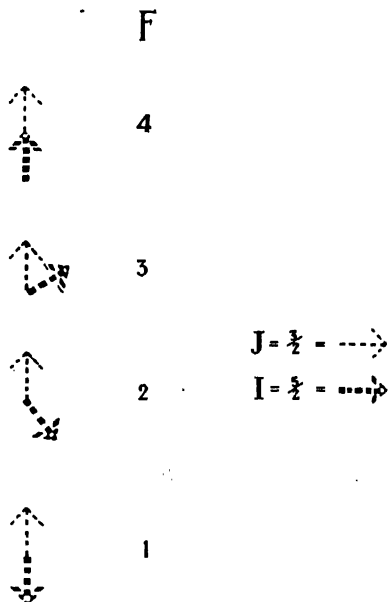
FIG. 13.—Illustrating the vector coupling between a nuclear spin $I = \frac{5}{2}$ with a $J = \frac{3}{2}$ to form four hyperfine structure levels.

double but becomes more complex. Since $J < I$, $2J + 1$ components are formed, so that with $J = \frac{3}{2}$ the term splits up into four components. We can see from Fig. 13 how these four levels can occur. The J value of the level is represented by the long thin arrow and the nuclear spin by the short thick arrow. In the highest level the two vectors are parallel, and in the lowest they are anti-parallel. In between these values, the vectors take up intermediate

positions that satisfy the cosine law. Expressed simply, this means that the angles between the vectors are such that the resultant vector F can have all *integral* values between 4 and 1. As shown in the diagram we obtain four levels with F values 1, 2, 3, 4, the smallest F value lying deepest. These levels will be so spaced as to obey the Landé interval rule, although this is not shown in the schematic vector diagram, but it is so drawn in Fig. 12. It is seen in this figure that the line $3s \cdot {}^2S_{1/2}$—$4p \cdot {}^2P_{3/2}$ has six components in its structure pattern. The components are grouped into two pairs of threes, owing to the smallness of the upper interval factor. If the interval factors of the upper terms are both very small compared with that of the lower term, the patterns cannot be completely resolved, and the structures of both the D lines will be doublets with the intensity ratio 5 : 7 and of approximately the same separation as was obtained when I was taken to be $\frac{1}{2}$. The above values, $\frac{1}{2}$, $\frac{5}{2}$, are taken for illustration only. The nuclear spin of sodium is now known to be $\frac{3}{2}$. This apparent similarity shows that the prime importance of experimentally resolving all the components of a line before a reliable estimate of the nuclear spin of the atom can be made, and when $I \gg J$ of checking the results by the examination of other terms.

When the nuclear spin of an atom is small, the term structures are simple, and the line patterns not very complicated, but when the spin is large, the terms with higher J values become quite complex and the line patterns correspondingly more so. Fortunately the interval factor in one of the terms of a line is often very much smaller than that in the other term and this introduces a considerable simplification into the line pattern which is formed.

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HYPERFINE STRUCTURE IN MANY-ELECTRON SPECTRA

Two-electron spectra

The calcium atom will be chosen to illustrate the structures expected in a two-electron system. No structure has so far been found in the odd isotope of calcium, but this is due to various causes which need not be considered here. As in the case of sodium the type of structure in the terms will depend upon the numerical value of the nuclear spin, but there are one or two features of special interest which are not dependent on this and these will be discussed first.

Reference to Fig. 6 shows that there are a number of sets of terms in calcium which go to different series limits and it is necessary to consider these separately. The most important terms are those which go to the $4s \cdot {}^2S_{1/2}$ limit. It will be remembered that the group of terms which go to this limit is produced when one of the valence electrons remains in a $4s$ orbit and the other moves to higher orbits. Since the electron configuration for each level of this group possesses a penetrating $4s$ electron, it will be expected that all the terms will show wide hyperfine structure splittings, where term splitting is possible. This is generally true, although in some terms the moment of the optical electron opposes that of the $4s$ electron and thereby reduces the coupling with the nucleus.

The terms going to the $4s \cdot {}^2S_{1/2}$ limit are $^1(SPD)$ and $^3(SPD)$ and of these the $^1S_0$ and the $^3P_0$ terms illustrate an important point. Since in these terms $J = o$, then $2J + I = I$, meaning that the multiplicity is one, i.e. the terms are single. This result is obvious, because the spin I can only add to a zero J value to form a single F value equal to I. *No matter what the nuclear spin may be, all spectral terms with J value equal to zero show no hyperfine*

structure.   For all the other terms **I** and **J** compound in the usual manner to form multiplets.   Suppose, for example, the nuclear spin is $\frac{3}{2}$, then the $^3P_0$ term will be single, the $^3P_1$ term will have three components, and the $^3P_2$ term will have four, as shown in Fig. 14.

F

$^3P_2$

$\frac{7}{2}$

$\frac{5}{2}$

$\frac{3}{2}$

$\frac{1}{2}$

I < J
2 I + 1 = 4

$^3P_1$

$\frac{5}{2}$

$\frac{3}{2}$

$\frac{1}{2}$

J < I
2J + 1 = 3

$^3P_0$

$\frac{3}{2}$

J < I
2J + 1 = 1
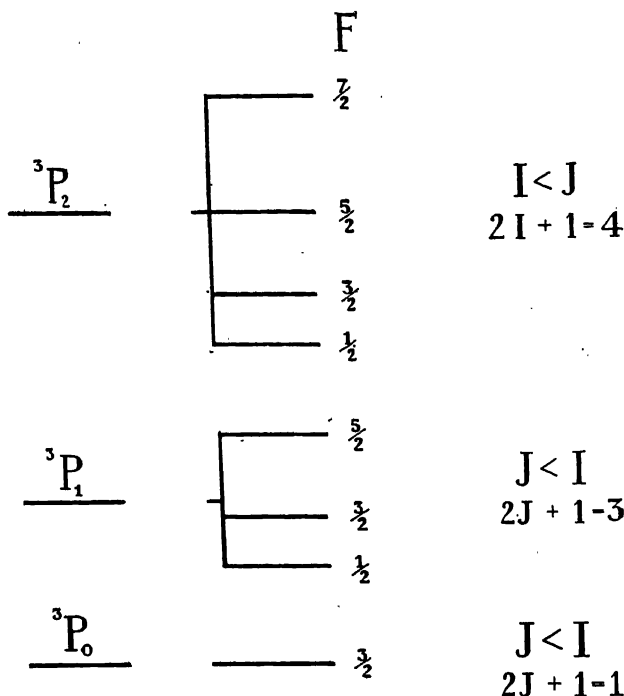
Fig. 14.—The hyperfine structures of ^3P terms when the nuclear spin is $\frac{3}{2}$.   The number is $2I + 1$ or $2J + 1$, according to which is the smaller.

Since all the terms which go to the $4s$. $^2S_{1/2}$ limit have a $4s$ electron in their configurations, the structures of all will be wide (excluding terms with $J = 0$).   It is seen from this that a line transition such as $4s$. $4p$. $^3P_2 - 4s$. $4d$. $^3D_2$

will have structures of the same order in both the upper and lower terms. The result is that the line pattern is complex, as, for example, in the case shown in Fig. 10. Most of the terms which go to the next limit, $3d \cdot {}^2D_{3/2}$, of the calcium atom, do not possess a penetrating $4s$ electron in their configurations, so that practically all the terms going to this limit have narrow structures, and the same is true of the terms which go to the next limit. Line transitions between one of the terms which go to the $4s \cdot {}^2S_{1/2}$ limit and one of the terms which go to another limit have their patterns much simplified, as was the case with the sodium lines in Fig. 12. *The lines which arise from transitions between two terms, neither of which possess unpaired s electrons in their configurations, often appear single, because the structure is so minute.* Generally speaking, the appearance of the structures is very dependent on the specific electrons in the configurations.

General vector method for many-electron spectra

A very convenient method for predicting the structures which arise in atoms with complex electron configurations has been developed by White.[1] This is an extension of the vector method which has already been used to show how gross structure multiplets arise. It was shown in Chapter III that the best way to see how the gross structure multiplets arise was by adding the vector representing the optical electron to the ion terms. The hyperfine structures are obtained by the simple extension of adding the nuclear spin vector to the terms already obtained in this manner. In a large number of cases only the configurations which possess a penetrating s electron show any structure in the terms, so that this type of term will be considered first.

If a configuration possesses a penetrating s electron, it can be shown that the coupling between the nuclear spin and the electron configuration is proportional to $\cos (\mathbf{Is})$ * and not, as in general, to $\cos (\mathbf{IJ})$. The direction of the

* s is the spin vector of the s electron. It is assumed throughout that LS coupling is used.

4

coupling between the nuclear spin and the s electron becomes of great importance, so that it is necessary to know exactly in which direction the s electron is pointing with reference to the other electrons of the configuration. For this reason the series limits must be known and the multiplet structure built up from the ion, in order that the coupling of the s electron can be followed carefully from term to term.
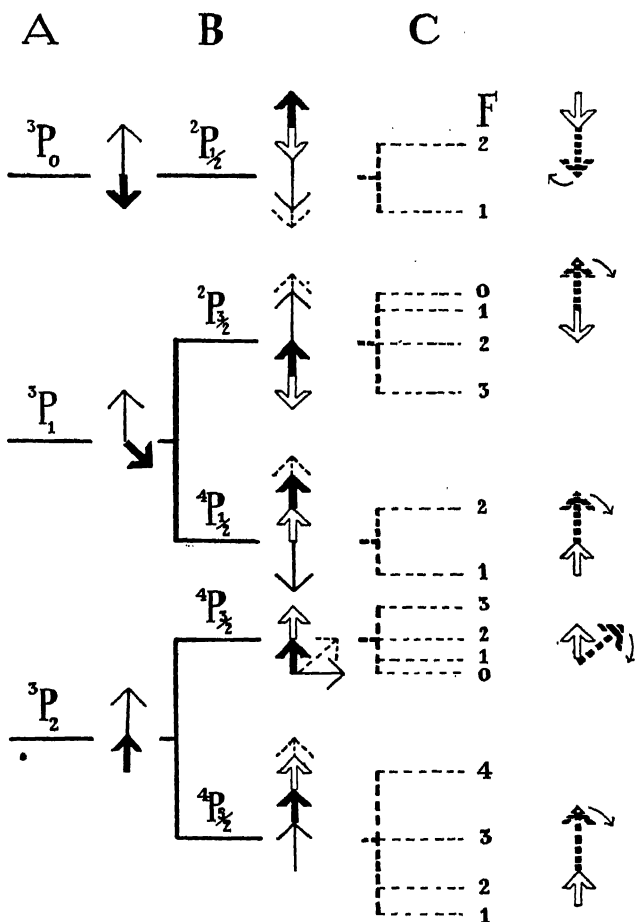
For the purpose of explaining the vector method, recourse will be made to Fig. 9, which shows how the ^{2}P and ^{4}P multiplets of the $4s^2 . 4p^4 . 5s$ configuration of Br I are formed.   The problem is to see how the addition of the nuclear spin affects the terms.   The terms are split up according to the J values, but the interval factors, on which the coarseness of the structures depend, are determined by the value of cos (**Is**).   White[2] assumes that the complex electron group $4s^2 . 4p^4 . 5s$ behaves as a unit and couples with **I** in the usual vector manner, the degree of coupling depending on the orientation of **I** and **s**.   The relative values of the interval factors, in a group of levels belonging to a gross structure term, are proportional to cos (**Is**) when cos (**IJ**) = 1.   That is to say, when the nuclear spin is set parallel to **J** the angle which **I** then makes with the spin **s** of the $5s$ electron determines the coarseness of the structure. From the properties of vectors we have

$$\cos (\mathbf{Is}) = \cos (\mathbf{IJ}) \times \cos (\mathbf{Js}),$$
and as $\cos (\mathbf{IJ}) = 1$ when **I** and **J** are parallel,
therefore $\cos (\mathbf{Is}) = \cos (\mathbf{Js})$.

As the coarseness of the structures is proportional to cos (**Is**) it must therefore also be proportional to cos (**Js**), hence the problem is to find the relative orientation of the spin of the s electron, with respect to the resultant J value of the term, and the angle between these vectors determines the coarseness of the structures.

As in the two electron spectra the *number* of hyperfine structure levels in any gross structure term is determined by the values of **I** and **J**.   There will be 2**I** + 1 or 2**J** + 1 levels according to which is the smaller value.   From the

A   B   C

$^3P_0$ $^2P_{1/2}$

$^3P_1$ $^2P_{3/2}$

$^4P_{1/2}$

$^4P_{3/2}$

$^3P_2$

$^4P_{5/2}$

F

2
1

0
1
2
3

2
1

3
2
1
0

4
3
2
1

$4s^2\, 4p^4$ $4s^2\, 4p^4\, 5s$

Br. II   Br. I

FIG. 15.—Vector coupling diagram showing how the hyperfine structures in the $4s^2 . 4p^4 . 5s$ configuration are produced by a nuclear spin of $\frac{3}{2}$.

Landé formula it is easy to see by subtraction of two levels
that the actual separation between two levels with quantum
numbers F + 1 and F is A(F + 1), A being the interval
factor for the term in question.   When I and s are parallel
cos (Is) = 1 so that A is positive.   When I and s are anti-
parallel cos (Is) = — 1 so that A is negative.   *A negative
value for* A *means that the hyperfine structures are inverted,
the highest* F *value lying deepest.*   The vector method will
now be applied to bromine in order to trace the various
possible couplings.

   Fig. 15 shows the vector combinations.   The notation is
exactly the same as in Fig. 9 * and in it A and B of Fig. 15
are identical with those of Fig. 9.   A shows the ³P terms
of Br II based upon the $4s^2 . 4p^4$ configuration and B shows
the $5s . ²P$ and $5s . ⁴P$ terms for Br I which are formed by
the addition of the $5s$ electron.   The vector process up to
this point has already been discussed in detail.   The ex-
perimental value for the nuclear spin of bromine is $\frac{3}{2}$ and
C shows the hyperfine structure levels (dotted) that should
arise when a spin of $\frac{3}{2}$ is added to the doublet and quartet
multiplets.   In order to simplify the complicated vector
diagrams, only the coupling between the nuclear spin and
the $5s$ electron is shown at the extreme right.   As before,
the thin dotted arrow in B shows the direction of J.   I
is set parallel to this, so as to conform to the rule that
cos (IJ) = 1 and in this position the interval factor is
proportional to the cosine of the angle between I and s.
The spin of the s electron is shown, as before, by the hollow
arrow, and the nuclear spin by the long thick dotted arrow.
The small curved arrow at the head of this implies that it
is to be compounded vectorially.

   Considering each term in detail it is seen that the $5s . ²P_{1/2}$
term has I parallel to s, and as $J = \frac{1}{2}$ the hyperfine structure
is therefore a wide normal doublet ; wide because the two
spin vectors assist, and normal since they act parallel.   In

   * In configurations of the type $4s^2 . 4p^4 . 5s$ and $4s^2 . 4p^4 . 5p$,
etc., it is often customary to omit the $4s^2 . 4p^4$ for the sake of
brevity, and only the optical electron $5s$ or $5p$, etc., is retained in
the term notation.

the next term $5s \cdot {}^2P_{3/2}$, the I and s oppose, so that the term
is inverted.   As $J = \frac{3}{2}$ a quartet term is formed, and the
structures are still comparatively large.   The $5s \cdot {}^4P_{1/2}$ term
is again a wide normal doublet.   The next term is $5s \cdot {}^4P_{3/2}$
and the nuclear spin acts at an angle with the s electron spin
so that a medium width quartet is produced.   Finally the
$5s \cdot {}^4P_{5/2}$ term has all the vectors parallel, so that a wide
quartet is formed.*

  The methods used to describe the coupling in the case
of a penetrating s electron can be applied to the case of a
non-penetrating p electron.   For instance, it is possible to
couple the $5p$ electron to the $4s^2 \cdot 4p^4$ core of Br II, but it
is found that the agreement with experiment is not very
good.   The supporting evidence for the s electron case
has been very well established in manganese, but different
investigations indicate that such a simple treatment is not
possible for p electrons.   It is quite certain that the p
electrons couple vectorially to give the correct *number* of
levels that theory demands.

  * There is reasonably good experimental verification for bro-
mine, the deviations being due to the incomplete LS coupling.
In manganese, which shows full LS coupling, the vector method
is completely verified.   Bromine has only been selected as an
example of a many-electron atom, for illustration purposes.

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[2] White, *Proc. Nat. Acad. Sci.*, **16**, 68, 1930.

ANALYSIS OF THE HYPERFINE STRUCTURES

Intensities of hyperfine structure components

Although it is true that severe perturbations may occur in hyperfine structure levels most of the spectra hitherto investigated seem to show the interval rule to be reasonably valid. The perturbations have been found in the structures of mercury, bismuth and aluminium, etc., and will be discussed later, but for the present purpose all that need be said is that in certain cases the structure in a term can be perturbed in such a manner that the interval rule fails. The intensities of the hyperfine structure components of a line are just as important as the intervals, and are of equal help in the analysis. Perturbations have been found in intensities, but so far these have not been very serious. The intensity disturbances are of two kinds. In one case they are due to the source being possibly too hot, or the pressure too high, with resulting self reversal effects. The other type of intensity perturbation is not understood, but will be discussed in the chapter dealing with perturbation.

The intensity rules which hyperfine structure components obey are important. These have been given by Hill [1] and since they are used so frequently in analysis, it has been considered worth while to reproduce them here. They form the basis of the graphical method of analysing structures, due to Fisher and Goudsmit,[2] which is useful in practical work. In the formulæ given below the following abbreviations are used: $In . (F . F + 1)$ means the intensity of a line transition from an upper term hyperfine structure F level to a lower term hyperfine structure level $F + 1$. The meanings of $In . (F . F)$ and $In . (F . F - 1)$ are then self-evident. In all cases the first F value refers to the upper term, and the second to the lower term. In the

formulæ themselves the following contractions are used for the sake of brevity.

$$P.(a.b.c.) \quad (a + b)(a + b + 1) - c(c + 1),$$
$$\cdot\, Q.(a.b.c.) \quad c(c + 1) - (a - b)(a - b + 1),$$
$$R.(a.b.c.) \quad a(a + 1) + b(b + 1) - c(c + 1).$$

All the transitions are those for which $\Delta L = \pm 1$, and there are three sets of formulæ according to whether ΔJ is equal to $+ 1$, 0, or $- 1$. These are set out in table form below. **A, B,** and **C** are constants determining the relative intensities of the gross structure lines but do not here concern us, since all the components for any one given line (i.e. single **J** transition) involve the same constant so that the intensity ratios in a hyperfine structure pattern are not dependent on the value of the constant.

On substituting in these formulæ one finds that *the transition* $\Delta F = 0 \to 0$ *always has zero intensity, and also that the total intensity of all the components to a given* **F** *level is proportional to* $2F + 1$. The formulæ appear rather cumbersome, but are actually simple to apply, and check themselves automatically, so that errors in calculation are avoided. Numerical intensity tables derived from these formulæ are now available.[3]

Irregular and regular line patterns

As a result of the intensity and interval rules, two types of line pattern are produced, and these may conveniently be called irregular and regular patterns. An irregular line pattern arises when both the upper and lower interval factors are of the same order. The line pattern becomes particularly complex when the hyperfine structure multiplicities are high. The irregular structures can only be analysed by seeking for frequency differences, as in the case of gross structure multiplets. When the hyperfine structure multiplet has been built up the **F** values of the terms are easy to find if $J > I$, but if $J < I$ the **F** values can usually only be obtained from the interval rule. If both **I** and **J** are already known, the analysis of a line is much simpler. However, when the **F** values have been found **I**

Transition.	$\Delta L = \pm 1$, $\Delta J = +1$	$\Delta L = \pm 1$, $\Delta J = 0$	$\Delta L = \pm 1$, $\Delta J = -1$
In. (F. F+1)	$A \cdot \dfrac{P .(F+1.J.I.).P.(F+2.J.I.)}{F+1}$	$B \cdot \dfrac{(F+1.J.I.).Q.(F.J.I.)}{F+1}$	$C \cdot \dfrac{Q .(F+1.J.I.).Q.(F.J.I.)}{F+1}$
In. (F. F.)	$A \cdot \dfrac{2F+1}{F(F+1)} \cdot P.(F+1.J.I.).Q.(F-1.J.I.)$	$B \cdot \dfrac{2F+1}{F(F+1)} \cdot [R.(F.J.I.)]^2$	$C \cdot \dfrac{2F+1}{F(F+1)} \cdot P.(F.J.I.).Q.(F.J.I.)$
In. (F. F-1)	$A \cdot \dfrac{Q(F-1.J.I.).Q.(F-2.J.I.)}{F}$	$B \cdot \dfrac{P.(F.J.I.).Q.(F-1.J.I.)}{F}$	$C \cdot \dfrac{P .(F.J.I.).P.(F-1.J.I.)}{F}$

can always be calculated. The best way to analyse a spectrum with many lines is to select the lines which involve terms wherein the J value is greater than the suspected I value. In all of these terms the multiplicity is $2I + 1$, so that I is determined when the line pattern has been analysed, and the interval rule can be applied as a check. It is often quite impossible to analyse the pattern of a line completely in this manner, because many structure components crowd together and cannot be resolved. The method has, however, been successfully used in very many cases, e.g. Cd, Tl, Pb, Hg.[4] etc. An example of an *irregular* pattern is shown in Fig. 16. The line pattern illustrated is that of $5s . {}^4P_{5/2}$— $5p . {}^4D_{5/2}$ in Br I. The nuclear spin is $\frac{3}{2}$ and for the purpose of illustration it is assumed that the interval factor of the upper term is $\frac{4}{5}$ that of the lower. The resulting pattern is complex, and no obvious apparent regularities exist in it.

In the irregular pattern described above, the irregularity arises from the fact that the two interval factors have nearly equal values. It often happens that only one term involves a penetrating s electron, and so produces a structure which is

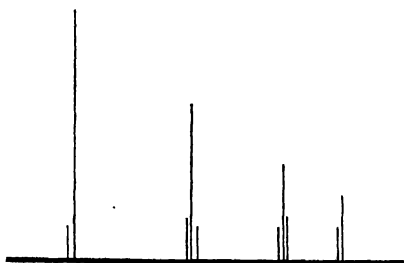very much coarser than the structure in the other term. When this is the case the line pattern becomes *regular* and has the appearance of a regular degraded series. For

Irregular
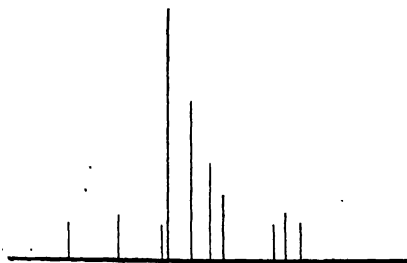
Interval factor ratio 5 : 4

Regular

Interval factor ratio 20 : 1

FIG. 16.—Dependence of the appearance of a fine structure line pattern on the fine structure interval ratio of the upper and lower terms.

example, the same line as above has the pattern shown in
Fig. 16 when the interval factor of the upper term is only
$\frac{1}{20}$ that of the lower. Owing to the natural widths of the
components, and partly because of imperfections in the
instruments used, the closely packed components cannot
often be separated, so that a regular quartet pattern will be
seen in the present example. It is clear that a regular
pattern will usually show the approximate structure of one
of the terms only (exceptions occur). In the present in-
stance the structure is that of the lower term, which involves
the s electron.* This *term* is therefore quartet in structure,
and as the J value is $\frac{5}{2}$, then I must be equal to $\frac{3}{2}$, because
a greater nuclear spin would have produced more com-
ponents. This line shows how a nuclear spin can often be
very easily obtained from one regular pattern. The scale
of the structures may be gathered from the fact that the
total width of the structure is about 0.4 cm.$^{-1}$.

Graphical method of analysis

In the regular " pseudo quartet " just described there
are actually *ten* components, and the appearance of the line
pattern becomes more and more complicated as the relative
value of the smaller interval factor increases, with respect
to the larger. In order to deal with complex patterns which
are incompletely resolved, a very valuable graphical method
of analysis has been proposed by Fisher and Goudsmit.[2]
For this graphical method I and the J of both terms must
be known for the line in question. It is often possible to
get I from the other data, e.g. from the structure of favour-
able lines or from band spectra, etc., so that the method is
generally applicable. The same line, namely

$$5s \cdot {}^4P_{5/2} - 5p \cdot {}^4D_{5/2}$$

of Br I, will be taken for an example of the use of this
graphical method.

The graph is shown in Fig. 17. Firstly the interval

* This example is taken from the actual experimental data in
Br I.

factors of both the upper and lower terms are made equal, and the complete multiplet drawn. The position of each component of the *line* pattern is plotted as a point along the line AB. Secondly, the upper term is completely inverted, the interval factor being kept unchanged, and the new resulting multiplet drawn. The position of each component of the new *line* pattern is plotted as a point along the line EF. Corresponding points, that is, points which represent the same F transitions, are joined up by straight lines. For preliminary visual analysis the widths of these lines are made roughly proportional to the intensities of the
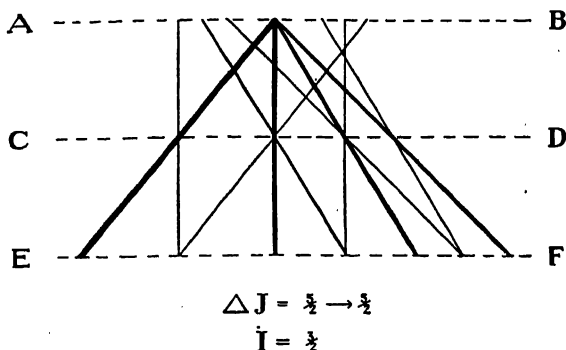

$$\triangle J = \tfrac{5}{2} \rightarrow \tfrac{5}{2}$$
$$I = \tfrac{3}{2}$$

Fig. 17.—Fisher-Goudsmit line complex for the transition $J = \tfrac{5}{2} \rightarrow \tfrac{5}{2}$. The nuclear spin is $\tfrac{3}{2}$ in this example.

transitions as calculated from Hill's formulæ. For the purpose of calculation, thin lines can be used, the actual intensity ratios being written in. The points which represent the upper limit of the whole graph, along AB, show the line pattern given by the two terms in question, when the interval factors of the two terms are identical; in other words, when the interval factor ratio is $+ 1$. Similarly, the points at the lower limit of the graph show the line pattern when the ratio of upper to lower interval factors is $- 1$. The horizontal line CD cuts the graph at the centre. Each line is cut at a point, and each point represents a component of the *line* pattern. This particular centre pattern is that

formed when the upper interval factor is equal to zero
[since CD lies midway between the lines AB and EF which
represent ratios of $+ 1$ and $- 1$ respectively]. For any
given ratio of interval factors, the *line* pattern is determined
by drawing a horizontal line through the graph at a point
between AE corresponding to this ratio. Thus, for example,
the line patterns of Fig. 16 were obtained by drawing hori-
zontals at points corresponding to interval ratios of $\frac{4}{5}$ and
$\frac{1}{20}$th respectively, the upper interval being the smaller in
both cases. When a line pattern has been measured all that
need be done is to fit it unambiguously into the graph, and
the values of both the upper and lower interval factors are
at once determined, although the resolution in the line
pattern may be incomplete.

REFERENCES

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[2] Fisher and Goudsmit, *Phys. Rev.*, **37**, 1057, 1931.
[3] White and Eliason, *Phys. Rev.*, **44**, 753, 1933.
[4] See papers by Schüler and co-workers, *Zeit. f. Phys.*, 1928.

TERM INTERVAL FACTORS

Coupling of two s electrons

From the calculated interval factors information can be obtained concerning the coupling processes of the individual electrons, and perturbation effects can be detected. Extensive theoretical calculations of the ratios of the interval factors of the different terms of a spectrum have been made by Goudsmit. From the experimental side, although data are lacking, enough has been found to show that the agreement between theory and observation is only partial. Discrepancies arise from the fact that the actual coupling process between a nucleus and an electron is unsufficiently understood. Fermi, Casimir, Breit, and Goudsmit[1] have all made different attempts to solve this mathematical problem, which presents grave difficulties.

There is general agreement for the case of the atom which possesses one valence electron, such as the alkali metals or ionised alkali earths. Theory shows that the interaction energy between the nucleus and the optical electron is of the form $E = A \cdot 1J \cdot \cos(1J)$. This leads to the Landé interval rule for hyperfine structures, and experimental observations support this strongly. Casimir showed that in the particular case of an *s* electron, the interaction energy is given by $E = A \cdot Is \cdot \cos(Is)$ and this fact has already been utilised. Following Casimir, Goudsmit has calculated the interaction energy for an atom which has two valence *s* electrons.[2] For example, all the $^3S_1$ terms of Ca I are terms of an atom which has two *s* electrons in its configuration. The interaction between the nucleus and the spins of the two electrons, s_1 and s_2, is

$$E = a_1 Is_1 \cdot \cos(Is_1) + a_2 Is_2 \cdot \cos(Is_2).$$

The energy is treated as the sum of two interaction energies,

one for each electron. Each electron obeys the law deduced by Casimir, and in the equation, a_1 and a_2 are the numerical proportionality factors for each electron.* The cosines are to be averaged over a complete electron revolution and when this is done the formula reduces to

$$E = IJ \,.\, \cos (IJ) \,.\, \left[\frac{a_1 s_1}{J} \,.\, \cos (s_1 J) + \frac{a_2 s_2}{J} \,.\, \cos (s_2 J) \right],$$

J, having the usual significance, being here the resultant of s_1 and s_2. Comparing this with the previous general equation, namely,

$$E = A \,.\, IJ \,.\, \cos (IJ),$$

it is evident that the two s electrons obey the same general law as one electron, if the interval factor A is replaced by the expression in square brackets. When the quantum values of the cosines are substituted in the expression for A we get

$$A = a_1 \,.\, \frac{J(J + 1) + s_1(s_1 + 1) - s_2(s_2 + 1)}{2J(J + 1)}$$
$$+ a_2 \frac{J(J + 1) + s_2(s_2 + 1) - s_1(s_1 + 1)}{2J(J + 1)},$$

since $s_1 = s_2 = \frac{1}{2}$, this reduces to

$$A = \tfrac{1}{2}a_1 + \tfrac{1}{2}a_2.$$

Thus, the term interval factor A is half the sum of the proportionality factors of the two electrons. Experimental verification of this has been possible in a few cases. Thallium I has been examined and the interval factors for the structures of the terms of the $6s \,.\, 7s$, $6s \,.\, 8s$, and $6s \,.\, 9s$, etc., configurations determined. From these it is possible to calculate the value of a_1 for the 6s electron and of a_2, a_3, a_4, etc., for the 7s, 8s, 9s, etc., electrons. The value of a_1 increases slightly as the second electron approaches the ionising limit because the screening effect of the second electron diminishes. a_1 tends to a limiting value which can

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* That is to say, the " interval factor " for the individual electron.

be calculated. In the Tl II atom, which possesses one electron in the $6s$ orbit, the value of a_1 should be identical with the limiting value of a_1 calculated from the Tl I spectrum. Allowance has to be made for the fact that the interval factor is proportional to z^2, where z is the degree of ionisation. More strictly the interval factor is proportional to $Z_i z^2$, but in a heavy atom Z_i is sensibly the same for the normal and the ionised atoms so that the coarseness of the structure is very nearly proportional to z^2.* The values of a_1 calculated from Tl I and Tl II agree within experimental error, so that the theory is supported.[3]

Interval factors for the general case

The general theory for the hyperfine structure interval factors in spectra, which show LS or jj coupling, has been worked out by Goudsmit,[4] and since it is not practicable to give any details of his calculations here, only a few of his results will be quoted. The calculations lead to different results in LS coupling and in jj coupling, the results being more satisfactory for the latter type. In LS coupling it is only possible to give the sum of the interval factors for all the terms of a multiplet group which have the same J value. For example, the ^1P and ^3P terms which arise from an $s \cdot p$ electron configuration are $^1P_1$, $^3P_0$, $^3P_1$, $^3P_2$. The interval factor for $^3P_0$ is zero, that of $^3P_2$ can be calculated, but only the sum of the interval factors for the two terms $^1P_1$ and $^3P_1$ is obtained from the formulæ, for they have identical J values.

The following table gives some of the more important results. a is the proportionality constant for the p electrons and b the constant for the s electrons in any configuration. The value of a or b is the same for all *equivalent* electrons. In the table only a selected group of results has been shown and for full details the original paper must be consulted.

The calculated values for the interval factors of spectra which show jj type of coupling are more satisfactory than

* This is obviously an important practical point, for the higher the degree of ionisation the coarser are the structures and therefore the easier to observe.

those for **LS** type, because the interval factor for every term is given separately. The s electron has the same proportionality constant **b** as in the **LS** coupling, but the p electrons are different. As **jj** coupling implies that each

TABLE III

Interval factors in **LS** *coupling*

Interval factor for p electron .   .   .   .   .   a
Interval factor for s electron .   .   .   .   .   b

Configuration.	J.	Interval Factor $= A.$
p and p^5	$\tfrac{3}{2}$	$A = \tfrac{8}{15}a$
	$\tfrac{1}{2}$	$A = 2\tfrac{2}{3}a$
p^2 and p^4	2	$\Sigma A = 1\tfrac{3}{5}a$
	1	$A = 0a$
p^3	$\tfrac{5}{2}$	$A = \tfrac{24}{25}a$
	$\tfrac{3}{2}$	$\Sigma A = 1\tfrac{13}{75}a$
	$\tfrac{1}{2}$	$\Sigma A = 2\tfrac{2}{3}a$
$p \cdot s$ and $p^5 \cdot s$	2	$A = \tfrac{3}{8}a + \tfrac{1}{4}b$
	1	$\Sigma A = 2a + \tfrac{1}{4}b$
$p^2 \cdot s$ and $p^4 \cdot s$	$\tfrac{5}{2}$	$\Sigma A = 1\tfrac{7}{25}a + \tfrac{2}{5}b$
	$\tfrac{3}{2}$	$\Sigma A = 1\tfrac{13}{15}a - \tfrac{1}{15}b$
	$\tfrac{1}{2}$	$\Sigma A = 0a + 1\tfrac{2}{5}b$
$p^3 \cdot s$	3	$A = \tfrac{4}{5}a + \tfrac{1}{6}b$
	2	$\Sigma A = 2a + \tfrac{7}{12}b$
	1	$\Sigma A = 2\tfrac{4}{5}a - \tfrac{1}{4}b$

electron has a separate j value, there are two types of p electron, namely $p_{1/2}$ and $p_{3/2}$. These two electrons differ because in the one the l and s oppose, so that j is equal to $\tfrac{1}{2}$, and in the other l and s are parallel in direction, so that j equals $\tfrac{3}{2}$. These two types of electron are different in so far as the $p_{1/2}$ electron is more penetrating than the $p_{3/2}$ electron, so that different proportionality constants enter

the formulæ for each. The constants will be called a'' for the $p_{1/2}$ electron and a' for the $p_{3/2}$ electron. According to theory these constants are not independent, but are related to the constant a of the p electron in LS coupling.

Theory gives

$$a' = \tfrac{8}{15}a,$$
$$a'' = \tfrac{8}{5}a,$$

therefore

$$a' = \tfrac{1}{3}a''.$$

As an example of the interval factors calculated for **jj** coupling, see Table IV. The first column in this table

TABLE IV

Interval factors in **jj** *coupling*

Interval factor for $p_{1/2}$ electron	a''
Interval factor for $p_{3/2}$ electron	a'
Interval factor for s electron	b

Configuration.	j.		J.	Interval factor.
p^2 and p^4	$\tfrac{3}{2}$ $\tfrac{3}{2}$	$\tfrac{3}{2}$ $\tfrac{1}{2}$	2	a'
			2	$\tfrac{3}{4}a' + \tfrac{1}{4}a''$
			1	$1\tfrac{1}{4}a' - \tfrac{1}{4}a''$
$p^2 \cdot s$ and $p^4 \cdot s$	$\tfrac{3}{2}$ $\tfrac{3}{2}$	$\tfrac{3}{2}$ $1\tfrac{1}{2}$	$\tfrac{5}{2}$	$\tfrac{4}{5}a' + \tfrac{1}{5}b$
	$\tfrac{3}{2}$ $\tfrac{1}{2}$	$\tfrac{1}{2}$ $\tfrac{1}{2}$	$\tfrac{3}{2}$	$\tfrac{3}{5}a' - \tfrac{1}{5}b$
			$\tfrac{1}{2}$	b
			$\tfrac{5}{2}$	$\tfrac{3}{5}a' + \tfrac{1}{5}a'' + \tfrac{1}{5}b$
			$\tfrac{3}{2}$	$\tfrac{9}{10}a' + \tfrac{3}{10}a'' - \tfrac{1}{5}b$
			$\tfrac{3}{2}$	$\tfrac{5}{6}a' - \tfrac{1}{4}a'' + \tfrac{1}{3}b$
			$\tfrac{1}{2}$	$\tfrac{5}{6}a' - \tfrac{1}{4}a'' - \tfrac{1}{3}b$
			$\tfrac{1}{2}$	b

gives the electron configurations, and the second column the **j** values of the individual electrons. The **j** value of the s electron is omitted, since it is always equal to $\tfrac{1}{2}$. In the third column the final resulting possible **J** values are shown, and opposite each **J** value (in the fourth column) is the calculated interval factor of the term. The terms with **J** = o are omitted as the interval factor for such a term is zero.

5

Interval factors in multiply ionised spectra

So far there is not a great deal of experimental evidence which has a bearing on the verification of the Goudsmit formulæ, since only few spectra have been thoroughly examined. Of interest are the results which have been obtained in the spectra of bismuth.[4] In bismuth the Bi I, Bi II, Bi III and Bi V spectra have all been studied. It has been possible to calculate the proportionality constants of the separate electrons when different neighbouring electrons are present. Thus, in Bi I the $6p^3$ and the $6p^2 \cdot 7s$ configurations give the values of $\mathbf{a''}$, $\mathbf{a'}$ and $\mathbf{b'}$ for the $6p_{1/2}$, $6p_{3/2}$ and $7s$ electrons respectively.* In Bi II the configurations examined were $6s \cdot 7s$, $6p \cdot 6d$ and $6p \cdot 7p$, so that the constants for the same electrons could be calculated, as well as those of $7p_{1/2}$ and $6d$. The Bi III spectrum gave data for the $6s \cdot 6p^2$ configuration, so that in addition the constant $\mathbf{b}$ for $6s$ was determined. Finally, the $6s$ configuration of Bi V also gave a value for the constant $\mathbf{b}$. A convenient summary of the results is shown in Tables V and VI :—

TABLE V

s electrons

Electron.	Constant.	Spectrum.			
		Bi I.	Bi II.	Bi III.	Bi V.
6*s*	**b**	1·6	1·6	1·8	2·6
7*s*	**b'**	0·116	0·352	0·472	—

For both the 6*s* and 7*s* electrons the value of the constant increases regularly with the increase in the degree of ionisation. This is due to the removal of screening outer

* Bismuth shows **jj** coupling in these terms.

TABLE· VI

p electrons

Electron.	Constant.	Spectrum.		
		Bi I.	Bi II.	Bi III.
$6p_{1/2}$	a''	0·375 0·390	0·430 0·565 0·462	0·66
$6p_{3/2}$	a'	0·008 0·026	0·028	0·01
$7p_{1/2}$	a'''		0·012	

electrons. Table VI gives a summary of the observations
made on the p electrons :—

It was possible to calculate a′ and a″ from more than one
term, and as seen in Table VI there is good approximate
agreement between these. The general conclusions to be
made from the tables are as follows :—

   (1) The constant for a given electron is bigger the higher
      the degree of ionisation, owing to the removal of
      screening effect as other electrons are removed from
      the configurations.

   (2) The constant for an electron falls rapidly in value
      when the total quantum number, n, of the electron
      increases.

   (3) The constant for the $p_{1/2}$ electron is *very* much greater
      than that of the corresponding $p_{3/2}$ * electron, the
      ratios of these constants being altogether much
      greater than the calculated value, 5 : 1.

   The fact that a″ is very much greater than 5a′, which
the simple theory at first predicts, is interesting. There

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  * The exact value of the $p_{3/2}$ electron constant was difficult to
determine, but the data showed unambiguously that it was
relatively quite small.

are two possible explanations, the second of which is much more likely than the first. It is possible that, owing to insufficient knowledge of the interaction processes, the equations are wrong, and the calculated values of a' and a" are not genuine. However, against this is the fact that the methods used to deduce the formulæ have given correct results when applied to gross structure multiplet data, and also to other hyperfine structure data. This explanation is therefore not very probable. A much more likely explanation has been suggested by Breit,[5] who has shown by means of a wave mechanics treatment, that in heavy atoms a $p_{1/2}$ electron behaves with respect to the nucleus as if it were a deeply penetrating electron. The effect is only marked in the heavier atoms, as it arises from second order corrections which are negligible when the atomic weight is small. If the $p_{1/2}$ electron behaves as if it were penetrating, it will therefore have associated with it a very large interval factor, comparable, in fact, with that of the s electron. As seen from the data in bismuth this is the case, so that Breit's theory offers a reasonable explanation of the relatively great value of a". It is, of course, of practical importance, as the penetrating property of the $p_{1/2}$ electron results in the production of structures far wider than at first expected on the simpler theory.

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ISOTOPE EFFECT

Isotope effect in bands

Up to the present any hyperfine structure effect arising from the existence of isotopes has been neglected in the discussion. The isotope effects have become very important from both the experimental and theoretical aspects, so they will be treated here in some detail. The first attempt to detect any isotope effect in line spectra was made by Aronberg,[1] who found that the wave-length of the lead line $\lambda 4508$ was slightly less in ordinary lead than in radium lead. He was not able to observe the true structure of the line, partly because the line was broadened in the source he used, and partly because the resolving power he employed was not very high. It was only later and more refined work that enabled the true isotopic effect in lead to be discovered.

The isotope effects in *line* spectra are always small (the effect in deuterium apart), but the isotope displacements which occur in some *band* spectra are very large indeed, and are easy to recognise. This arises because the positions of the vibration heads of an electronic band system depend upon the moment of inertia of the nuclei of the molecule, and are very sensitive to changes in the value of this moment of inertia. For example, boron has the two isotopes B_{10} and B_{11} so that the band spectrum of the oxide consists of two sets of bands, one due to $B_{10}O_{16}$ and the other to $B_{11}O_{16}$. The different boron atoms have different moments of inertia because of their different weights. The band constants differ and as a result the band heads of the one system are displaced from those of the other by large amounts. Displacement of the order of 20 cm.$^{-1}$ are not unusual in band spectra, from which it is seen that experimental observation of isotope effect in band spectra is much

easier than in line spectra. The spectroscopic study of isotopes has, of course, to be carefully co-ordinated with Aston's mass spectrograph data.

Mass effect in line spectra

The first effect successfully found and interpreted was the *simple mass effect*. This was predicted by Bohr's theory, which showed that the positions of the lines of a spectrum depend upon the mass of the nucleus of the atom. A change in the mass of the nucleus causes a slight shift in the position of a line, so that if an atom consists of two isotopes, with different masses, all the lines of the spectrum will be duplicated. Calculation shows that the expected duplication will usually be very small, and must be sought for as a hyperfine structure. As an example of the approximate method of calculation, the mass isotope effect to be expected in neon, which was the first to be observed, will be calculated.

In general the series terms of a spectrum can be fitted into a Hick's formula which is of the form

$$E = \frac{Rz^2}{\left(n + a + \dfrac{b}{n^2}\right)^2}.$$

In this formula a and b are numerical constants, n is the effective quantum number, z is the effective nuclear charge, and R is Rydberg's constant. The value of the Rydberg number is not strictly a constant, but involves the reduced mass of the electron, which is $\dfrac{mM}{m + M}$, where m and M are the mass of the optical electron, and the whole nucleus respectively. Neon mainly consists of two isotopes of masses 20 and 22.* The electron systems in these atoms are identical, hence the series will also be identical, but as the Rydberg numbers differ slightly, one of the series will be relatively displaced, i.e. all the lines will show a structure. The calculation of the displacement is as follows.

* Isotope 21 is too weak to be taken into consideration here.

The frequency of a line is the difference of energy between two terms divided by Planck's constant, so that $\nu = \mathbf{R}(\mathbf{A})$, where ν is the frequency, $\mathbf{R}$ the Rydberg constant, and $\mathbf{A}$ is of the form

$$\mathbf{A} = \frac{z^2}{h}\left[\frac{1}{\left(n_1 + a + \dfrac{b}{n_1^2}\right)^2} - \frac{1}{\left(n_2 + a + \dfrac{b}{n_2}\right)^2}\right].$$

For the isotopic constituents of a line $\mathbf{A}$ is constant, since it does not involve the nuclear mass. The only variable factor is $\mathbf{R}$. It follows then, that

$$\nu_{20} = \mathbf{R}_{\cdot \cdot}(\mathbf{A}),$$
$$\nu_{22} = \mathbf{R}_{\cdot 2}(\mathbf{A}),$$

hence $\qquad \nu_{22} - \nu_{20} = (\mathbf{R}_{22} - \mathbf{R}_{20})(\mathbf{A}.)$

But $\nu_{22} - \nu_{20}$ is the difference between the two isotopic components of the line, i.e. the isotopic separation $\Delta\nu$, hence

$$\Delta\nu = \mathbf{R}_{22} \cdot (\mathbf{A})\left[1 - \frac{\mathbf{R}_{20}}{\mathbf{R}_{22}}\right] = \nu_{22}\left[1 - \frac{\mathbf{R}_{20}}{\mathbf{R}_{22}}\right].$$

But as the Rydberg constant is proportional to $\dfrac{m\mathbf{M}}{m + \mathbf{M}}$, the reduced mass of the electron, it follows that

$$\frac{\mathbf{R}_{20}}{\mathbf{R}_{22}} = \frac{m \cdot \mathbf{M}_{20}}{m + \mathbf{M}_{20}} \times \frac{m + \mathbf{M}_{22}}{m \cdot \mathbf{M}_{22}},$$

i.e. $\qquad \dfrac{\mathbf{R}_{20}}{\mathbf{R}_{22}} = \dfrac{1 + \dfrac{m}{\mathbf{M}_{22}}}{1 + \dfrac{m}{\mathbf{M}_{20}}} = 1 + m\left(\dfrac{1}{\mathbf{M}_{22}} - \dfrac{1}{\mathbf{M}_{20}}\right)$

to a first approximation. If M is the mass of the hydrogen atom the masses of the neon isotopes are $20M$ and $22M$ respectively, so that

$$\frac{\mathbf{R}_{20}}{\mathbf{R}_{22}} = 1 - \frac{m}{M}\left(\frac{1}{220}\right).$$

Therefore $\Delta\nu = \nu\dfrac{m}{M}\dfrac{1}{220}$ (ν being an approximate mean

value of ν_{20} and ν_{22}. It is sufficiently accurate for the purpose to take the mean frequency of the line without consideration of hyperfine structure).

The ratio $\dfrac{m}{M}$ is the ratio of the mass of an electron to that of a proton and is equal to $\frac{1}{1836}$, so that

$$\Delta\nu = \nu \cdot \frac{1}{1836} \cdot \frac{1}{220} = \frac{\nu}{400,000}$$

in approximate round numbers. For a line whose wave-length is 5000 A the displacement would therefore be about 0.05 cm.$^{-1}$. The isotopic displacement can be calculated for any other line in a similar manner.

The mass isotope displacement effect has been thoroughly investigated in neon and it has been shown that $\dfrac{\Delta\nu}{\nu}$ is nearly constant for lines of the same series. The value of the displacement is consistently a little greater than that predicted by the simple theory, but the motion of the nucleus accounts for this.

There is no room for doubt that, for each line, the two components are produced by the different isotopes, as Hertz [2] has clearly shown. In ordinary neon the isotopes are present in the ratio 9 : 1, the lighter atom being the more abundant. The hyperfine structure components should have the intensity ratio 9 : 1, which is observed in practice. Hertz succeeded in separating the isotopes of neon by means of a continuous diffusion process so that in the two end samples obtained, the ratio of $Ne_{20} : Ne_{22}$ was 1 : 1 and 100 : 1 respectively. The spectrum of the first sample showed each line as a doublet, both components having the same intensity. On the other hand, the second sample showed each line to be quite single, as the other component was too faint. This affords a direct proof of the isotopic origin of the hyperfine structures in neon.

The simple mass isotopic effect is usually very difficult to observe, as it decreases rapidly with increase in atomic weight. For instance, in the bromine line 6122 A the dis-

placement should only be 0·004 cm.$^{-1}$. The mass isotope effect has been detected in a number of atoms including H,[3] Li, Ne,[4] Cl,[5] K,[6] and possibly Br,[7] and more recently boron. The most important of these is the exceptional case of hydrogen, for the spectroscopic detection of the isotope displacement effect was the original method whereby the existence of deuterium was demonstrated.

The mass effect in hydrogen is abnormally large in relation to that shown by other isotope mixtures because of the favourable mass ratio. It will be seen from the previous treatment that $\Delta \nu = \nu m / 2M$, and for H_α this amounts to as much as some 4 cm.$^{-1}$, an amount easily resolved even by prism spectrographs.

Mixed odd and even isotopes

In the heavy and moderately heavy atoms the simple mass isotope displacement is usually far too minute to be observed. A new effect arises when the atom consists of a mixture of isotopes of even and odd atomic weight. This effect was first observed by Schüler and Brück [8] in the cadmium spectrum. Cadmium consists of six isotopes, two of which have odd and the other four even atomic weights.

The two odd atomic weight isotopes have each a nuclear spin but no mass displacement can be detected in any of the lines, as the effect is far too small. At the optical centre of gravity of the structure of each line lies a single very strong component. Intensity measurements reveal the fact that the intensity ratio of this single component, to the summed intensities of all the other components in the line, is the same as the abundance ratio of the even to the odd isotopes. It was found possible to account for all the components *excluding* the central strong one by assuming $I = \frac{1}{2}$. There seemed to be no doubt about the interpretation of the weak lines, since the number of components and their intensities fitted a spin of $\frac{1}{2}$. It was, therefore, suggested by Schüler and Brück that the *even isotopes possess no nuclear spin, so that each contributes a single line, the lines all falling together at the optical centre of gravity of the spin hyperfine structure pattern*

and appearing as one. The even isotopes form a single line because the mass displacements are too small to be measured.
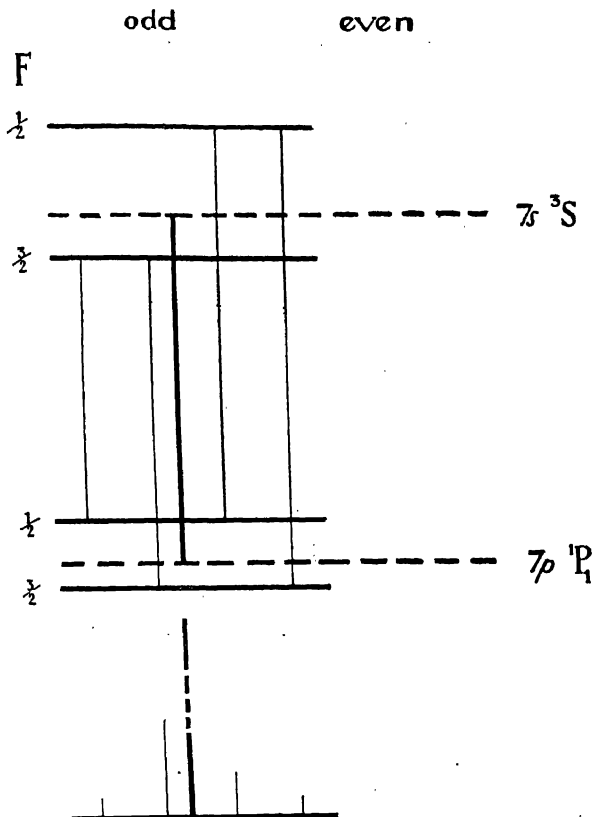

FIG. 18.—Undisplaced isotope line due to the even isotopes in the cadmium hyperfine structures. The thin lines show the doublet multiplet due to the odd isotopes, and the thick line represents the unaffected lines from the even isotopes all falling at the centre of gravity of the hyperfine structure pattern.

Obviously the intensity ratio of the central compound component to that of the total sum of the others must be the abundance ratio of the even to the odd isotopes.

The way in which the cadmium hyperfine structures arise is shown in Fig. 18. The line illustrated is $7p$. $^1P_1$—$7s$. $^3S_1$. Attention may be drawn to the fact that the structures in cadmium are inverted, which means that the biggest F values are deepest. *This inversion is not to be confused with the term inversion which was previously discussed when* $\cos (Is) = -1$. The *whole* of the hyperfine structures are inverted, as if the nuclear magnetic moment arose from a negatively charged nucleus. Referring again to the diagram, the doublet multiplet arising from the split terms of the odd atoms is shown. The quantum weight of a hyperfine structure level is $2F + 1$, so that the dotted lines indicate the centres of gravity of the split terms. The dotted lines are the positions the terms occupy in the even atoms, for the effect of a nuclear spin is to split up a term about its centre of gravity. The thick vertical line represents the transitions in the even atoms, the final resulting line pattern being shown below. It is to be observed that the isotope effect just described only arises from the fact that different isotopes have *different nuclear spins*. There is no displacement of the lines of isotopes which have the same spin.

Isotope displacement effect

The so-called isotope displacement effect is of quite a different nature and was first found in the thallium structures by Schüler and Keyston.[9] Thallium consists of two isotopes, 205 and 203, the lighter of which is the more abundant in the ratio 2·3 : 1. Both isotopes have the nuclear spin of $\frac{1}{2}$. Fig. 19, showing the analysis of the line $6s$. $7s$. $^3S_1$—$6s$. $7p$. $^1P_1$, reveals the displacement effect. The line transitions due to the more abundant isotope, 203, are shown to the left at A, and those due to the less abundant, 205, are shown dotted at B. The observed line pattern is drawn, as usual, below. The analysis was carried

out by the use of frequency differences and the careful
observation of intensities.   Each transition in A is 2·3 times
as strong as the corresponding transition in B, so that the
analysis is quite certain.   Furthermore, there is no doubt
about the value of the nuclear spin which has been obtained
from other lines which show no isotope effect.   The transi-
tions B should fall into the same system as A, but have been
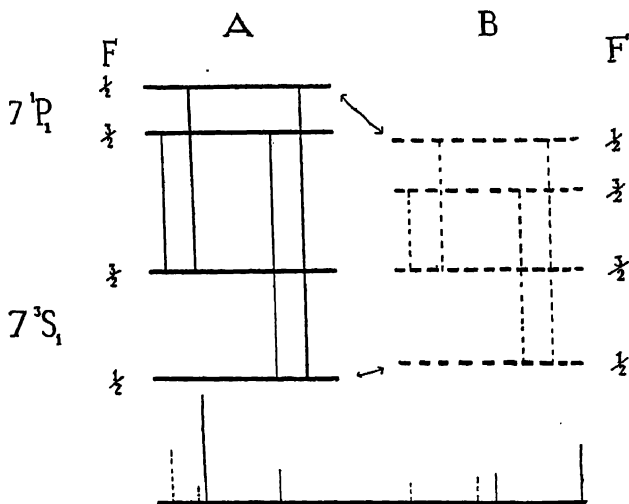displaced to the right in order to clarify the diagram.

FIG. 19.—Isotope displacement effect in thallium.

A study of the line shows just what the displacement
effect is.   The structure of the $^1P_1$ term is the same in both
isotopes, but there is a small measurable difference in the
widths of the $^3S_1$ structures.   *The most marked effect is the
bodily displacement of the whole of the $^1P_1$ term in one of the
isotopes,* that is to say, the *centre of gravity* of the term has
been displaced without much appreciable alteration of the
size of the structure.   The result of this is a bodily shifting
of the whole *line* pattern of the one isotope with respect to

the other. The displacement is far greater than that calculated for the simple mass effect and must be ascribed to some other cause.

### Displacement in odd and even isotopes

Displacement effects in atomic species containing a mixed group of odd and even isotopes have been observed in mercury, zinc, platinum and others. Most of the salient features appear in the platinum arc spectrum studied by Tolansky and Lee.[17] The platinum isotopes revealed by the mass spectrograph are 192, 194, 195, 196, 198, of which 192 is very weak and will be disregarded. The analysis of the structure of a typical line (λ5390·8) is shown in Fig. 19 (a) 1. The analysis in Fig. 19 (a) 2 is derived from a comprehensive term scheme including the numerous line transitions involving thirty-three separate terms. The dotted levels and transitions refer to the odd isotope 195 which has a nuclear spin $\frac{1}{2}$. The unbroken levels and transitions refer to the even isotopes 194, 196, 198. The two patterns are separated for clarity, and the scale for the even isotopes increased for clarity in Fig. 19 (a) 2.

It will be seen that these do not fall together, as in cadmium, but suffer a small displacement (about 0·044 cm.$^{-1}$), the amounts for 194-6 and 196-8 being the same, within limits of error of observation (some 2 units).

The intensity ratios of the even isotope lines agree with the mass spectrograph abundance ratios. A point of considerable interest, as yet not explained, is that the " centre of gravity " of the odd isotope pattern (195) does not fall exactly half-way between the 194 and 196 even isotope lines. The extent of this effect is shown in Fig. 19 (b) in which the " centre of gravity " of isotope 195 is shown dotted. This effect appears in other platinum lines, such as λ5369·0 also shown in Fig. 19 (b).

The case of mercury is also interesting. There are six isotopes of measurable intensity, namely, 198, 199, 200, 201, 202, 204. Both the odd isotopes have nuclear spins, but the point of interest is that the spins differ, that of 199

being $\frac{1}{2}$ and that of 201 being $\frac{3}{2}$. (Other atoms also have different spins for different isotopes.) The hyperfine struc-
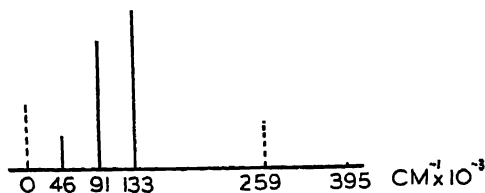
19 (a).1
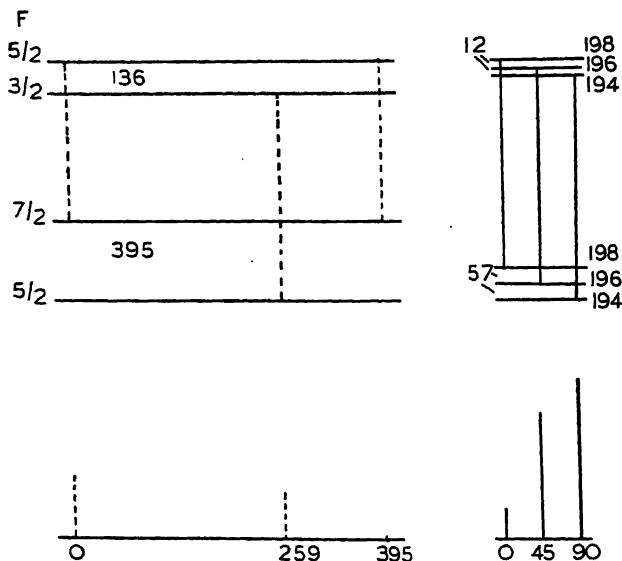
19 (a).2

FIG. 19 (a).—Isotope effect in a platinum line.

ture terms in 201 are all inverted relative to those of 199.

Some of the terms of mercury illustrate isotope displacement of a more complex nature than that encountered in
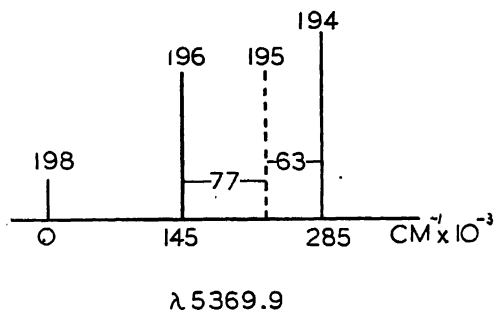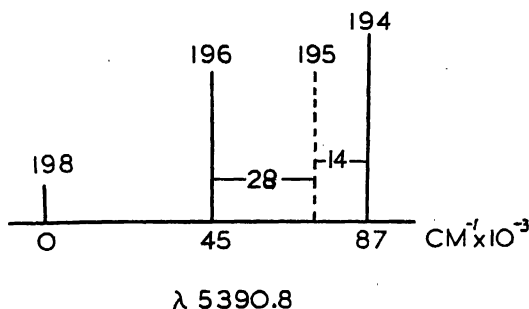

λ 5390.8

λ 5369.9

FIG. 19 (b).—Asymmetry of centre of gravity of odd isotope in platinum.

thallium. Fig. 20 shows an analysis of 4358 A in Hg I. The four even isotopes do not coincide, but are relatively displaced (see hatched lines). The observed intensities of

these even isotope lines are in excellent agreement with the abundance ratios. The two odd isotopes each show the pattern expected from their respective spins, but in addition, the centre of gravity of each pattern is displaced. In the figure the straight lines belong to 199 and the dotted lines to 201. The hatched lines are 198, 200, 202, 204, respectively.
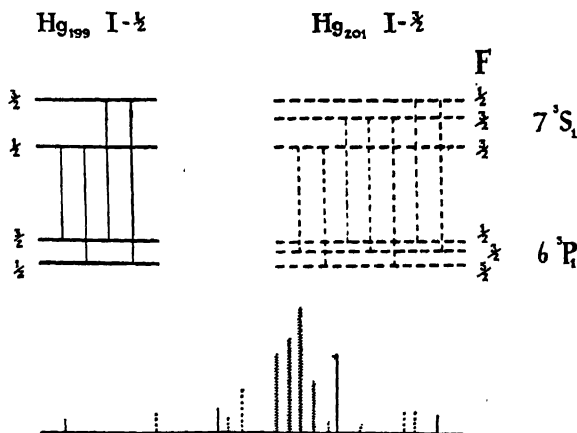
FIG. 20.—Hyperfine structure of the mercury line 4358 A, showing the isotope displacements. The hatched lines arise from the even isotopes, the dotted lines from 201, and the straight lines from 199.

The isotopic displacement effect implies that the binding energies of the electrons are different in different isotopes. Fig. 21 shows the displacements which have so far been found in the Hg I spectrum.[10] The $^1S_0$ series has big displacements in the deepest term, and these rapidly diminish up the term sequence so that by $8\,^1S_0$ the displacements can no longer be measured. The $7\,^3S_1$ term also shows a small displacement which diminishes so rapidly up the term sequence that it can no longer be measured in higher terms. Two other terms show a displacement effect, namely the complex $6\,^1P_1$ term arising from the $5d^9 \cdot 6s^2 \cdot mp$ con-

figuration, and the 8 $^1P_1$ term of the ordinary configuration. The complex term is the term shown at the extreme left of the diagram. It follows, therefore, that regular displacements, falling off up a term sequence, only occur in the $^1S_0$ and $^3S_1$ terms. The 8 $^1P_1$ term shows displacement because it is perturbed. This will be discussed in a later chapter.
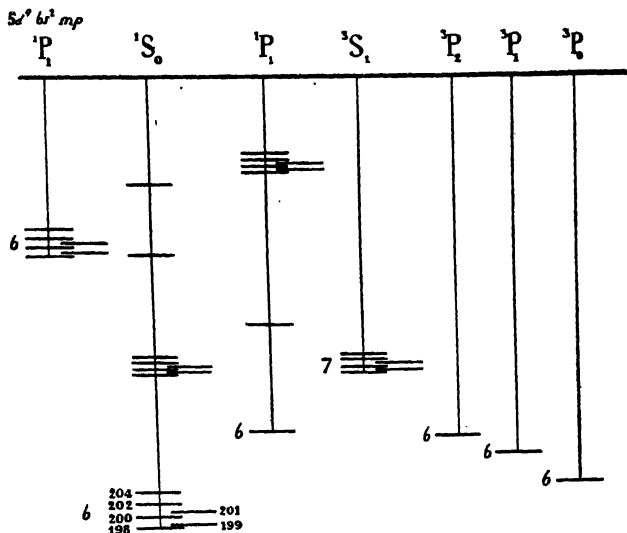

FIG. 21.—Isotope displacements in the terms of the Hg I spectrum. The displacements in all the terms are in the same order as those numbered in 6 $^1S_0$.

The relative displacement of the individual isotopes in one term is also of interest. Fig. 22 shows the displacements arising in the complex 6 $^1P_1$ term. The displacements in all the terms are similar, except that the scales are different. The deepest term is that of 198, and the even isotopes are approximately the same distance apart, in the order of increasing atomic weights. These are shown

6

above the line in Fig. 22. Below the line the centres of gravity of the structures of the odd isotopes are drawn, and it is seen that although the distance between the centres of gravity is practically identical with the distance between a
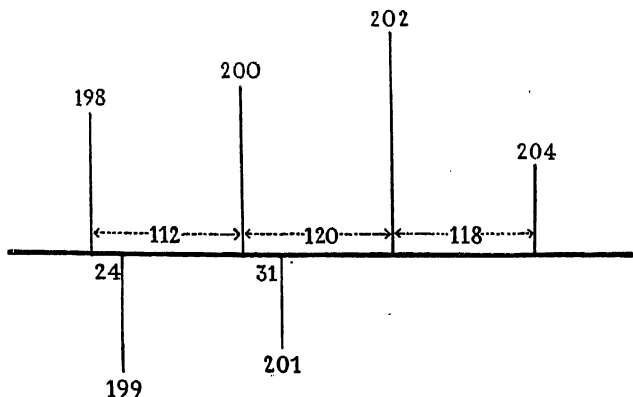

FIG. 22.—Relative displacements of isotopes in the 6 $^1P_1$ term of Hg I.

pair of even isotopes, both the even isotopes are displaced towards the next lightest atom.

Dependence of isotope displacement effect on electron configuration

Isotope displacements have now been measured in a large number of spectra including Hg I,[14] Hg II, Tl I, Tl II, Pb I, Pb II,[11] Cu II,[12] Zn II,[15] Wo I,[16] Pt I,[17, 18]

The most comprehensive data are those given by Tolansky and Lee for the Pt I spectrum.

Table VII shows the configurations in some different spectra in which even isotope displacement has been detected and measured.

Before discussing this table it should be noted that perturbed terms in mercury and in lead show anomalously large isotope displacement and as the lead spectra are suspected to be severely perturbed, they are best left out in discussion.

Of the remaining term configurations, it is significant that all but two types are of the kind known as " complex " configurations, i.e. configurations in which an inner shell is broken by removal of an electron, e.g. $5d^9 . 6s^2 . mp$.

TABLE VII

Pb I	$6s^2 . 6p . mp$	$6s^2 . 6p . md$	
Pb II	$6s^2 . 6p$	$6s^2 . 6s \quad 6s^2 . 6d$	
Hg I	$6s . ms$	$5d^8 . 6s^2 . mp$	
Hg II	$5d^9 . 6s^2$		
Tl I	$6s^2 . mp$		
Tl II	$5d^9 . 6s^2 . 6p$		
Cu II	$3d^9 . 4s^2$		
Wo I	$5d^4 . 6s^2$		
Zn II	$3d^9 . 4s^2$		
Pt I	$5d^9 . 6s$	$5d^9 . 7s$	$5d^8 . 6s^2$
	$5d^9 . 6p$	$5d^8 . 6s . 7s$	$5d^8 . 6s . 6p$

Two additional features emerge, (1) displacements diminish usually on going up a sequence, (2) a configuration with an s^2 group shows a very large effect.

$5d^8 . 6s^2 \left\{ \begin{array}{l} \\ \\ \\ \end{array} \right.$	$^3F_2$	200
	$^3F_3$	203
	$^3F_4$	203
$5d^8 . 6s . 7s$	$^5F_4$	103
$5d^8 . 6s . 6p$	$^5F_4$	107
$5d^9 . 6s$	$^3D_2$	117
$5d^9 . 6p$	$^3F_3$	56
$5d^9 . 7s$	$^3D_2$	12
$5d^{10}$	$^1S_0$	0

The details for the platinum spectrum given by Tolansky and Lee deserve further discussion and a small selected group of the results is shown above. The displacements are in units of 1 cm.$^{-1} \times 10^{-3}$.

It is assumed (although this is not absolutely certain) that the completely closed shell $5d^{10}$ has virtually no displacement effect (if it has, the displacement in this term is to be added to that of the others).

The largest displacements (203) are found in the ^3F multiplet involving the $5d^8 . 6s^2$ group. The displacements in the groups involving only one $6s$ electron are about *half* of these. It seems clear that *the effects of the two $6s$ electrons in $6s^2$ are additive and do not compensate in the manner usually characteristic of gross structure multiplicity.*

As in other spectra, the higher sequence members show much smaller effects, e.g. 117 displacement for $5d^9 . 6s . {}^3D_2$ and 12 for $5d^9 . 7s . {}^3D_2$.

Within a multiplet the displacements *do not appear to be at all dependent on* J. This is shown by a comparison of the nuclear spin hyperfine structure interval factors (A) and the corresponding isotope displacements (D) shown below for the ^3F group.

Term.		A.	D.
$5d^8 . 6s^2$	$^3F_2$	80	200
	$^3F_3$	52	203
	$^3F_4$	31	203

The manner in which A varies with J whilst D remains constant is clearly demonstrated.

The analysis of the isotope displacement effects is considerably complicated by the effect of local term perturbation and much work remains to be done before a detailed theory can be developed.

It seems quite established that the Bohr mass effect cannot be invoked to explain the large displacements found in the heavier atoms. The mass effect for a mass M increasing to $M + 2$ is proportional to $1/M^2$ which excludes simple mass modification of Rydberg constant as a possible explanation.[13]

Displacement due to different isotope magnetic moments

A relatively infrequent isotope effect, which produces displacement in the line pattern but not displacement in the terms, is that found in antimony by Tolansky.[19]   A typical case is illustrated in Fig. 22 (*a*).
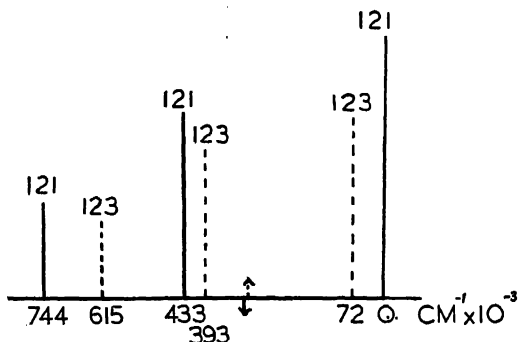

FIG. 22 (*a*)—Isotope effect in antimony.

There are two antimony isotopes, 121, 123, with abundance ratio almost 5 : 4.   The spin of one isotope is $\frac{5}{2}$, that of the second being $\frac{5}{2}$ (or $\frac{7}{2}$?).   The isotopes have quite different nuclear magnetic moments, that of 121 being 1·37 times that of 123.   Thus the pattern of every line consists of a hyperfine structure multiplet for isotope 121 and superimposed within this is a pattern from isotope 123, having about $\frac{4}{5}$ the intensity and shrunk down to $\frac{5}{7}$ of the scale of the former.   As a result, the patterns for lines of even moderate J value are exceedingly complex.   For example, aΔJ $= 3 \rightarrow 2$ line has twenty-eight components and these form so complex a pattern that in a specific case but ten could be resolved from the general overlap.   In Fig. 22 (*a*), the continuous lines represent isotope 121 and the dotted lines isotope 123.

But simple lines, such as ΔJ $= 0 \rightarrow 1$, reveal the isotope effect in a clear manner.   A typical case is shown in Fig. 22 (*a*).   This is the line 6806, involving wide structure arising from a **J** $= 1$ term.

The pattern for each isotope is a regular triplet, that for 123 being shown dotted.

The difference in magnetic moment is responsible for the separation of the two patterns, whose centres of gravity almost coincide so that there is no term displacement effect in the sense already discussed formerly.

It has been established by calculations that all isotope displacement effects cannot be ascribed to nuclear motion. Such an explanation can account only for the displacements in the lighter atoms. Displacements are in effect due to deviations from Coulomb's law. A physical interpretation is possible by describing this in terms of an effective *nuclear radius*. The difference between two typical isotopes of mass M and M + 2 is that two extra neutrons are packed into the nucleus and clearly the nuclear volume might be expected to increase. The increased volume leads to an alteration in nuclear-electron interaction and this produces the isotope displacement. Schüler and Schmidt suggest that the nucleus with the larger volume has less electrostatic energy than that with smaller volume, since both have identical charge, and this leads to the displacement.[20]

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PERTURBATIONS IN HYPERFINE STRUCTURES

In the present chapter an account will be given of the perturbation effects which have now been found in many structures. Well marked perturbations have been observed in Hg I,[1] Al II,[2] Bi IV,[3] etc. The suggestion was first made by Schüler and Jones that those of Hg I are analogous to the gross structure series perturbations which were first explained by Shenstone and Russell.[4] From a study of two electron spectra, the latter investigators conclude that in a spectrum with two terms, produced by different electron configurations, but with identical L S and J values, these terms perturb each other, even although they may be widely separated. The perturbation shows itself as an apparent repulsion between the terms. Paschen [2] and Goudsmit and Bacher [5] have gone further in the explanation of the effect. It is found that two types of perturbation exist. One is probably similar to the Shenstone-Russell effect, but the other perturbation apparently takes place when the gross structure multiplet separation is of a similar order to that of the hyperfine structure separation. Each will be discussed in turn.

Total widths of the structures

Let us first consider the total widths of the structures which arise from two isotopes of an atom. In most cases when an atom has two odd isotopes, both have the same nuclear spin and the same nuclear magnetic moment μ. In Hg the isotopes 199 and 201 have different spins, namely $\frac{1}{2}$ and $\frac{3}{2}$, the spin being negative in the latter. It can be shown,[6] that the total splitting of a term, namely the distance

between the extreme F levels for any given gross structure term is ΔW, where

$$\Delta W = \mu . H_0 . \frac{2J + 1}{J} \text{ when } J \geqslant I, \text{ and}$$

$$\Delta W = \mu . H_0 . \frac{2I + 1}{I} \text{ when } I \geqslant J.$$

In these formulæ H_0 is the magnetic field of the optical electron at the nucleus, and only depends on the term, whilst μ is a nuclear function. The ratio of the magnetic moments of 199 and 201, namely μ_{199} and μ_{201}, can be obtained by comparing the total widths of the structures of the two isotopes in a given term. In a particular case,[1] when $J = 1$, for 199,

$$\Delta W_{199} = 3\mu_{199} . H_0,$$

and for 201,

$$\Delta W_{201} = \tfrac{3}{8}\mu_{201} . H_0.$$

Therefore,

$$\frac{\mu_{199}}{\mu_{201}} = \frac{8}{9} . \frac{\Delta W_{199}}{\Delta W_{201}}.$$

From five terms with $J = 1$ it was found that the total widths of the structures are identical, but inverted relative to each other, i.e.

$$\frac{\Delta W_{199}}{\Delta W_{201}} = -1, \ .$$

which gives

$$\frac{\mu_{199}}{\mu_{201}} = -\frac{8}{9} = -0.89.$$

For terms with $J = 2$ it also follows that

$$\frac{\Delta W_{199}}{\Delta W_{201}} = \frac{\mu_{199}}{\mu_{201}} = -0.89.$$

These numerical relations hold well in all the terms examined, except in the $6\ ^1D_1$ term, where $\frac{\Delta W_{199}}{\Delta W_{201}} = -0.74$ instead of -1, and in the $6\ ^3D_2$ term, where $\frac{\Delta W_{199}}{\Delta W_{201}} = -1.08$ instead of -0.89. It is of interest to note that the next

member of the series of the latter term, namely $7\ ^1D_2$, has a normal ratio for the spread of the structures in the two isotopes.

The centres of gravity of the structures of lines involving these terms are displaced and this must be connected in some way with the above effect. In lines which do *not* show any appreciably large isotope displacement, the centres of gravity of the structures due to the two odd isotopes practically coincide with the null line formed by all the even isotopes. However, in lines which involve the $6\ ^1D_2$ term, the centres of gravity of the structures of the two isotopes practically coincide, *but both are displaced from the null line by an amount roughly equal to* 0·04 *cm.*$^{-1}$, *the displacement being to the red*. It will be remembered that $\dfrac{\Delta W_{199}}{\Delta W_{201}}$, calculated from this term, is too large. On the other hand, in lines involving $6\ ^3D_1$ the centres of gravity of the structures due to the two odd isotopes again coincide, but this time *are displaced from the null line to the violet by about* 0·06 *cm.*$^{-1}$.

This term gives too small a value for $\dfrac{\Delta W_{199}}{\Delta W_{201}}$. Both these anomalies arise from a perturbation which will now be discussed.

Perturbation of F *levels*

The perturbation in this case arises from the accidental fact that the two terms $6\ ^1D_2$ and $6\ ^3D_1$ are very close to one another. The structures in these terms are approximately 0·8 cm.$^{-1}$ wide and the distance between the centres of gravity of these structures is only 3 cm.$^{-1}$. The whole of the perturbations can be completely explained if it is assumed that *hyperfine structure levels with the same* F *value repel one another*. The way this perturbation occurs in the 199 isotope is shown in Fig. 23. A very convenient fixed point exists from which the perturbations can be measured, this is the position of the even isotopes. The F value of the even isotope terms in $6\ ^1D_2$ is 2 (since I = 0) and the F value of the even isotope terms in $6\ ^3D_1$ is 1, and as these

F values are different, there is no repulsion effect between
the even isotope components.   Further there is no measur-
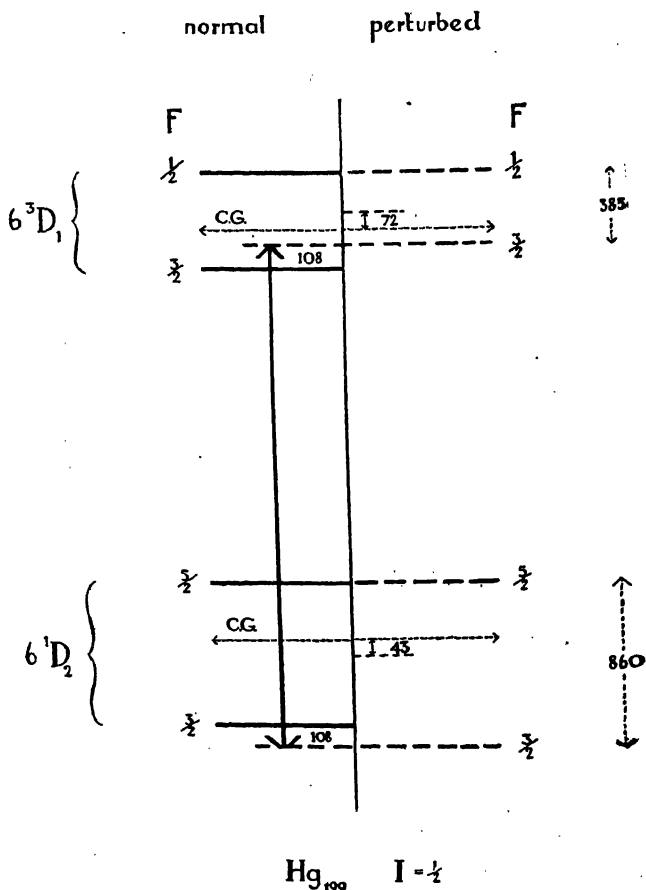able isotope displacement in both terms, so that the even

FIG. 23.—Perturbation effect in the 199 isotope of mercury.

isotopes in both terms form single fixed points. The fixed points are shown in the diagram by the thin dotted lines which are marked C.G., since they are the centres of gravity of the unperturbed terms. Considering now the 199 isotope, the two hyperfine structure levels which have the same F value, in this case $\frac{3}{2}$, repel each other from the zero points by the same amount. The thick lines at the left of the figure show the normal levels, and the dotted lines at the right the perturbed levels. The drawing is to scale, the units * being millicentimetres^{-1}. The thick vertical arrow shows the two levels which repel each other, and it will be observed that, as the upper levels are inverted, the upper structure becomes *narrower*, and the lower structure *wider*. Since the levels of 6 $^3D_1$ shrink together because of the perturbations, the centre of gravity of the hyperfine structure pattern due to Hg_{199} is moved *up* 72mcm.$^{-1}$. Correspondingly, as the lower term is widened, the centre of gravity of the Hg_{199} pattern is moved *downwards*, in this case 43 units, so that a net displacement towards the violet, is obtained.

The perturbations in the structures of isotope 201 are a little more complex because the nuclear spin is greater and thus the hyperfine structure multiplicities are also higher. The perturbations are shown in Fig. 24, the notation being the same as in the previous figure. For clarity the displacements of the centres of gravity have been omitted. Only the levels with F equal to $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$ find their counterparts in both the upper and lower structures, so that the repulsion only takes place between these levels. As in the previous case, the levels with the same F values are both repelled from the unperturbed position by the same amount. For $F = \frac{1}{2}$ the upper level moves up, and the lower down, by a distance equal to a = 42 mcm.$^{-1}$. The $F = \frac{3}{2}$ levels displace by b = 56 mcm.$^{-1}$ and the $F = \frac{5}{2}$ levels by c = 78 mcm.$^{-1}$. *The value of the displacements is such that the interval rule still holds in the upper term structure ;* owing to the fact that the lower $F = \frac{7}{2}$ level is not perturbed the

* A convenient unit to adopt is the millicentimetre^{-1}, which can be written as mcm.$^{-1}$.

interval rule necessarily breaks down for the lower term
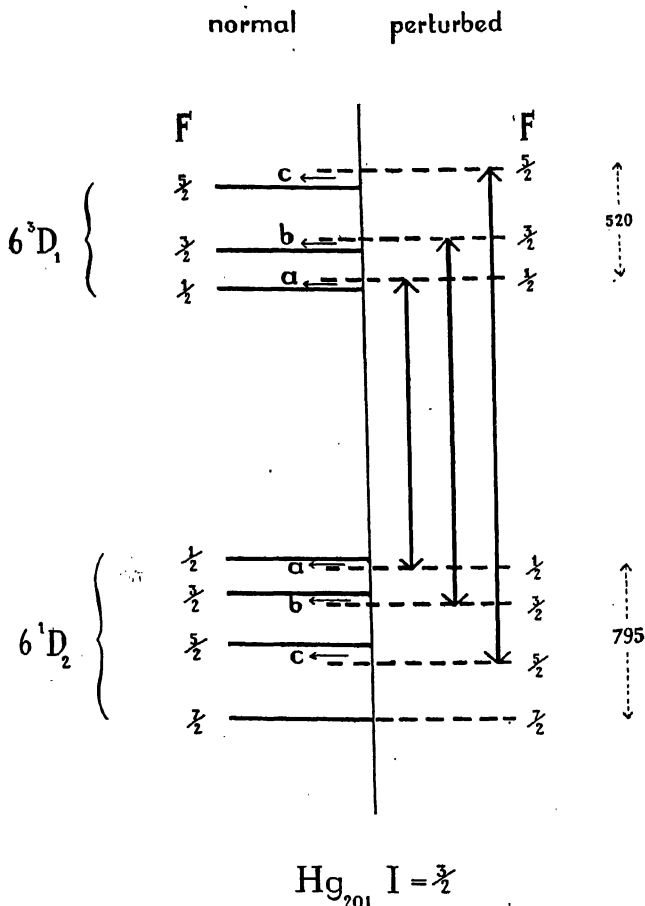as a whole.

FIG. 24.—Perturbation effect in the 201 isotope of mercury,
showing how the interval rule breaks down in the perturbed
6 $^1D_2$ term.

It is at once apparent from the values of a, b, c that the perturbation is some function of F, and as the perturbation is different in Hg_{199} the effect must also be dependent on the value of I or $g(I)$. Fig. 24 shows that the $F = \frac{1}{2}$ levels are much closer together than the $F = \frac{5}{2}$ levels, yet the perturbation in the latter pair is greater than in the former. Furthermore, the value of the displacement in the $F = \frac{3}{2}$ levels of Hg_{199} is about twice that of the displacement in the $F = \frac{3}{2}$ levels of Hg_{201}, although the latter are nearer together.

The perturbation effect just described explains all the anomalies in the term structures. The values of the total splittings of the terms are so affected that the ratios of $\frac{\Delta W_{199}}{\Delta W_{201}}$ are no longer normal, but the observed values agree with the calculated values when the perturbation is taken into account. The displacements of the centres of gravity of the structures of the odd isotopes are completely accounted for, and the break-down of the interval rule in the $6\,^1D_2$ term of Hg $_{201}$ isotope is thus explained. *Perturbation only seems to take place between levels with the same L and F values.*

Isotopic displacement perturbation

Reference to Fig. 21 reveals the interesting fact that the $8\,^1P_1$ term in Hg I has an anomalously large isotope displacement effect in all the isotopes. This is doubtless associated with the fact that this term is perturbed by the $5s^2 . 6d^9 . 6p . {}^1P_1$ term shown at the left of Fig. 21. The whole of the $^1P_1$ series of Hg I is perturbed from the $8\,^1P_1$ term upwards, because of the presence of the $6\,^1P_1$ term from the complex configuration. As both terms have the same J value, the even isotopes have the same F value and so perturb each other. The perturbation is proportional to the mass of the atom so that the even isotope lines are regularly displaced. It is possible that some observed isotope displacements are perhaps related to perturbations.

Theory of perturbations

Extensive perturbations in Al II have been observed, and explained by Paschen.[2] According to Paschen, when the coupling between I and J (which determines the total widths of the hyperfine structure pattern of a term) is of the same order as the coupling between L and S (which determines the gross structure multiplet width) then a perturbation sets in. Effectively it is as if the nuclear magnetic field were sufficiently strong to affect the coupling between L and S, and vice versa, the electron magnetic field perturbs the IJ coupling. (More correctly, it is as if the Paschen-Back effect sets in on both the structures.)

The theory is beautifully verified by Paschen's observations in Al II. By examining successive members of a series, he showed that the perturbations begin to occur when the expected hyperfine structure pattern becomes wider than the multiplet separation. In the term series $4 \, {}^1F_3 - nG$, the lower series members up to 8G show no trace of structure, but beyond this, the terms 8G, 9G, 10G, 11G, show a hyperfine structure practically independent of n. The terms change in character and partake of both singlet and triplet properties. Furthermore the J values are completely undetermined between the values 5, 4, 3. The constancy of the structures is due to the fact that the g electron contributes very little for the high n values, and in effect the structures depend only on the value of the structure of the $3s \, . \, {}^2S_{\frac{1}{2}}$ term of Al III, i.e. on the structure of the ion of Al II.

If the above theory is correct, then it can be shown that forbidden lines should appear, i.e. the J selection principle should be violated, and this is found to be the case. Paschen also explains the perturbation in Hg I as a Zeeman effect. The perturbing terms here are $6 \, {}^1D_2$ and $6 \, {}^3D_1$, and as long ago as 1902 Runge and Paschen found that these terms showed asymmetrical Zeeman patterns. Parchen was of the opinion that the repulsion effects reported by Schüler and Jones are not a resonance phenomenon, but are just what would take place if the perturbation was a Zeeman

effect. Goudsmit and Bacher [5] have given a more extended theoretical treatment of the effect. The theory predicts the existence of forbidden transitions when perturbation occurs. Where only two levels of the same F value are apparently repelled, then if δ is the displacement from the null position and if Δ is the actual separation of the two perturbing levels, the ratio of the intensity of forbidden transitions I to allowed transitions I_0 is given by the formula $\dfrac{I}{I_0} = \dfrac{\delta}{\Delta + \delta}$. In Hg I this is only true for the odd isotope terms, for there is no perturbation in the even isotopes. It follows from the theory that transitions should take place from 6 $^1D_2$ to terms with $J = 0$, and from 6 $^3D_1$ to terms with $J = 3$. It is of particular interest that the line $6d \cdot {}^1D_2 - 7p \cdot {}^3P_0$ actually occurs and when examined for hyperfine structure it is found that the even isotopes are entirely missing.[7] This is a valuable proof of the theory which demands forbidden transition in the odd isotopes only.

Deviations from the interval rule which are due to the nucleus are discussed in Chapter XII.

Intensity perturbations

The intensities in hyperfine structure components can, of course, be modified by self absorption, but this cannot be regarded as a true perturbation effect. Intensity perturbations have only been found in a hollow cathode discharge in cadmium when the exciting currents are high.[8] In certain lines the transitions which involve the highest F value of the upper term are relatively strengthened. This effect is not due to self absorption, and has not yet been explained.

<div align="center">REFERENCES</div>

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[2] Paschen, *Sitz. d. Preusz. Ak. Wiss.*, **32**, 502, 1932.
[3] McLay and Crawford, *Phys. Rev.*, **44**, 986, 1933.
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[6] Kallman and Schüler, *Erg. d. Ex. Naturwiss.*, XI, 138, 1932.
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[8] Schüler and Keyston, *Zeit. f. Phys.*, **71**, 143, 1931.

NUCLEAR SPINS

NUCLEAR spins have now been determined for a large number of isotopic species. The results are given in Table VIII, A, B, C, D below. These are collected from an extensive literature.

Atoms can be divided into four classes according to their nuclear mass and charge, thus :—

A, *odd* atomic weight, *odd* charge.
B, *odd* atomic weight, *even* charge.
C, *even* atomic weight, *odd* charge.
D, *even* atomic weight, *even* charge.
Class A atoms possess an odd *proton*.
Class B atoms possess an odd *neutron*.
Class C atoms possess an individual single neutron-proton pair.
Class D atoms possess mostly a mass divisible by 4, i.e. alpha particle mass as unit.

The various tables will now be discussed. *In no case has a spin exceeding* $\frac{9}{2}$ *been recorded.* The last column shows the nuclear magnetic moments in Bohr magnetons. These will be discussed in a succeeding chapter. The statistical distribution of the spins is of interest and will also be discussed later.

Class A atoms

In all these odd atomic weights observed spins are half integral multiples of $h/2\pi$ and spins vary from $\frac{1}{2}$ to $\frac{9}{2}$ with no apparent regularity.

Class B atoms

Again all observed spins are half integral and in the same range as Class A atoms. In quite a considerable proportion

NUCLEAR SPINS AND MAGNETIC MOMENTS

TABLE VIII (A)

A. ODD MASS AND ODD CHARGE, i.e. ODD PROTON

Mass.	Charge.	Symbol.	Spin ($h/2\pi$).	Mag. Mom. (Bohr Magneton).
1	1	H	$\frac{1}{2}$	2·7896
7	3	Li	$\frac{3}{2}$	3·2532
11	5	B	$\frac{3}{2}$	2·686
15	7	N	$\frac{1}{2}$	0·280
19	9	F	$\frac{1}{2}$	2·625
23	11	Na	$\frac{3}{2}$	2·215
27	13	Al	$\frac{5}{2}$	3·63
31	15	P	$\frac{1}{2}$	—
35	17	Cl	$\frac{5}{2}$	1·368
37	17	Cl	$\frac{5}{2}$	1·136
39	19	K	$\frac{3}{2}$	0·391
41	19	K	$\frac{3}{2}$	0·215
45	21	Sc	$\frac{7}{2}$	4·6
51	23	V	$\frac{7}{2}$	—
55	25	Mn	$\frac{5}{2}$	—
59	27	Co	$\frac{7}{2}$	2·3
63	29	Cu	$\frac{3}{2}$	2·5
65	29	Cu	$\frac{3}{2}$	2·6
69	31	Ga	$\frac{3}{2}$	2·0
71	31	Ga	$\frac{3}{2}$	2·5
75	33	As	$\frac{3}{2}$	1·5
79	35	Br	$\frac{3}{2}$	2·6
81	35	Br	$\frac{3}{2}$	2·6
85	37	Rb	$\frac{5}{2}$	1·340
87	37	Rb	$\frac{3}{2}$	2·741
93	41	Cb	$\frac{9}{2}$	3·7
107	47	Ag	$\frac{1}{2}$	− 0·1
109	47	Ag	$\frac{1}{2}$	− 0·2
113	49	In	$\frac{9}{2}$	5·49
115	49	In	$\frac{9}{2}$	5·43
121	51	Sb	$\frac{5}{2}$	3·7
123	51	Sb	$\frac{5}{2}$ ($\frac{7}{2}$)	2·8
127	53	I	$\frac{5}{2}$	2·8
133	55	Cs	$\frac{7}{2}$	2·558
139	57	La	$\frac{7}{2}$	2·8
141	59	Pr	$\frac{5}{2}$	—

TABLE VIII (A)—(Continued)

Mass.	Charge.	Symbol.	Spin ($h/2\pi$).	Mag. Mom. (Bohr Magneton).
151	63	Eu	$\frac{5}{2}$	3·4
153	63	Eu	$\frac{5}{2}$	1·5
159	65	Tb	$\frac{3}{2}$	—
165	67	Ho	$\frac{7}{2}$	—
175	71	Cp	$\frac{7}{2}$	2·6
181	73	Ta	$\frac{7}{2}$	—
185	75	Re	$\frac{5}{2}$	3·3
187	75	Re	$\frac{5}{2}$	3·3
191	77	Ir	$\frac{3}{2}$	—
193	77	Ir	$\frac{3}{2}$	—
197	79	Au	$\frac{3}{2}$	0·2
203	81	Tl	$\frac{1}{2}$	1·45
205	81	Tl	$\frac{1}{2}$	1·45
209	83	Bi	$\frac{9}{2}$	3·6
233	91	Pa	$\frac{3}{2}$	—

TABLE VIII (B)

B. ODD MASS AND EVEN CHARGE, i.e. ODD NEUTRON

Mass.	Charge.	Symbol.	Spin ($h/2\pi$).	Mag. Mom. (Bohr Magneton).
9	4	Be	$\frac{3}{2}$	− 1·176
13	6	C	$\frac{1}{2}$	0·701
67	30	Zn	$\frac{5}{2}$	0·9
83	36	Kr	$\frac{9}{2}$	− 1·0
87	38	Sr	$\frac{9}{2}$	− 1·1
111	48	Cd	$\frac{1}{2}$	− 0·65
113	48	Cd	$\frac{1}{2}$	− 0·65
117	50	Sn	$\frac{1}{2}$	− 0·9
119	50	Sn	$\frac{1}{2}$	− 0·9
129	54	Xe	$\frac{1}{2}$	− 0·8
131	54	Xe	$\frac{3}{2}$	0·7
135	56	Ba	$\frac{3}{2}$	0·837
137	56	Ba	$\frac{3}{2}$	0·936
171	70	Yb	$\frac{1}{2}$	0·4
173	70	Yb	$\frac{5}{2}$	− 0·7
195	78	Pt	$\frac{1}{2}$	0·6
199	80	Hg	$\frac{1}{2}$	0·5
201	80	Hg	$\frac{3}{2}$	− 0·6
207	82	Pb	$\frac{1}{2}$	0·6

TABLE VIII (C)

C. Even Mass and Odd Charge (Neutron-Proton Pair)

Mass.	Charge.	Symbol.	Spin ($h/2\pi$).	Mag. Mom. (Bohr Magneton).
2	1	D	1	0·854
6	3	Li	1	0·820
10	5	B	1	0·597
14	7	N	1	0·402
40	19	K	4	— 1·290

TABLE VIII (D)

D. Even Mass (Multiple of 4) and Even Charge

Mass.	Charge.	Symbol.	Spin ($h/2\pi$).	Mag. Mom.
4	2	He	0	—
12	6	C	0	—
16	8	O	0	—
32	16	S	0	—

of cases the magnetic moment is negative. This means that the nuclear-electron coupling is such that the hyperfine structure multiplets are completely inverted, the lowest **F** value usually lying deepest.

Class C atoms

This is a limited group. *In each case but the last the spin is 1 and the magnetic moment small.* It is reasonable to conclude that these lighter elements are built up from alpha particles with an odd neutron-proton pair added in each case. The magnetic moment is small and as a result hyperfine structures are too small to be measured. Both mechanical

and magnetic moments have been derived by methods other than those using hyperfine structures, in particular the magnetic deflection method has been very successful here.

Class D atoms

The atoms in this group have mass divisible by four. The spins are known to be zero with certainty from the fact that alternate lines are missing in the band spectra. Absence of hyperfine structure is not evidence of zero spin, but only of small nuclear magnetic moment ; an obvious fact, not universally recognised.

These spin values appear to indicate that alpha particles are basic building stones in nuclear construction.

An exceptional case of considerable interest is that of the potassium isotope mass 40 and charge 19, whose spin is given by magnetic deflection experiments as 4. This isotope is radioactive, with a very long decay period and beta-decay theories predict in such a case a large nuclear spin.

It is clear how incorrect is the frequently made assumption of zero spin for even mass. One might in fact state categorically instead that *even mass has integral spin which may or may not be zero* and indeed, as far as the evidence goes, appears only to be zero when the mass is divisible by 4 and the charge is even.

Statistical distribution of nuclear spin

Tolansky has reported a striking statistical difference in the distribution of nuclear spin of class A and class B atoms. This is shown in Fig. 25, which is a histogram showing for the two classes the spins of nuclei plotted against the number having those spins.

For the *odd proton class* above the distribution of spins is roughly that of a probability distribution curve.

For the *odd neutron class* below the distribution is strikingly different. It is clear that *low* spin values are favoured. This fact has been used to support a theory of nuclear spin which attributes the spin to an odd nuclear particle (theory

of Landé).   It was shown by Inglis that in such a case low spin values will arise in the odd neutron atoms.
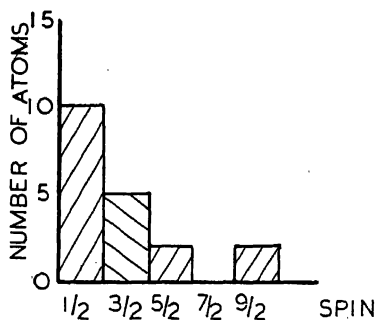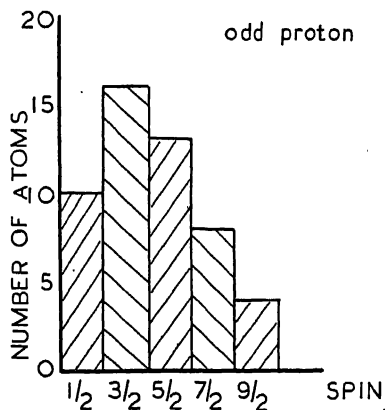

FIG. 25.—Statistical distribution of nuclear spin.

NUCLEAR MAGNETIC MOMENTS

Magnetic and mechanical moments

We have already seen that the number of hyperfine structure levels in a term depends upon the value of I (provided that $I > J$). The width of the structure is determined, not by the *mechanical* moment, but by the *magnetic* moment of the nucleus. The effect of the nuclear mechanical spin is to create a nuclear magnetic field, which, coupling with the magnetic field produced by electron spin and orbital moment, gives the observed hyperfine structure pattern. The coupling theory has been dealt with in earlier chapters, but it is apparent that the size of the structure is dependent on the value of the nuclear magnetic moment. It will be shown later that in favourable cases this moment can be calculated from the observed patterns.

It will be recalled that the phenomenon of alternating intensities in band spectra arises from the existence of the *mechanical* moment I, whilst the widths of the hyperfine structures in the line spectra depend (amongst other things) upon the *magnetic* moment, i.e. on $g(I)$. Cases occur where an atom has a definite value of I as revealed by the band spectrum, yet no structures are observable, even in terms involving penetrating electrons. The conclusion must be made that the nuclear magnetic moment is small, so that no measurable structures exist. Associated with this is the problem of the reported zero spins for so many even isotopes. All that has really been observed, in *line* spectra, is that the even isotope lines show no structure. Band spectrum observations in He^4, C^{12}, O^{16}, S^{32}, prove that these four even atoms have zero spin, but attention may be drawn to the fact that these atomic weights are divisible by four. The assumption has been made that because these four even atoms are known to possess a zero spin, therefore the absence

of structure in other even isotope lines is also an indication of zero spin. This may not be true. It is quite possible that some even isotopes may have a mechanical spin but have extremely small nuclear magnetic moments. This is certainly true in some cases. This point cannot be over-emphasised, for unfortunately a tendency has grown up in which workers have unquestioningly assumed that absence of structure in even isotopes means zero spin.

Magnetic moment of the proton

The value of the magnetic moment of the proton is of particular interest, for theories of nuclear spin have been proposed which attribute the nuclear magnetic properties to protons and neutrons. It is apparent from the relatively small values of the nuclear spins ($\frac{9}{2}$ is the greatest observed with certainty) that only a very limited number of the nuclear protons or neutrons contribute to the spin. It may be possible, therefore, to correlate the value of the proton or neutron magnetic moment with nuclear magnetic moments in general, and indeed attempts to do this have been made.[1] A value of the magnetic moment of the proton can be deduced from very simple considerations. Both electron spin and proton spin are $\frac{1}{2}$, but as the protonic mass is 1836 times as great as the electronic mass, the magnetic moment of the spinning proton should be $\frac{1}{1836}$ that of the electron, i.e. $\frac{1}{1836}$ of a Bohr magneton. It has been pointed out before that the doublet separation in gross structure multiplets is due to the *electron* magnetic moment, so that on this basis, to a first approximation, hyperfine structures should be 2000 times smaller than the gross structure width.

The magnetic moment of the proton was first determined experimentally by Estermann and Stern [2] by means of a refined improvement of the Stern-Gerlach experiment. In this experiment a beam of atoms or molecules is passed through an intense non-homogeneous magnetic field, and the deflections that the beam experiences enable the magnetic moment of the particles of the beam to be calculated. Molecular hydrogen exists in two states, para and ortho,

in one of which the electron spins oppose and in the other
assist. A beam of hydrogen was used in which the electron
spins cancel out, so that the magnetic moment due to the
protons could be observed, and it was found that the proton
magnetic moment was some 2·8 times that expected, i.e.
$\frac{2·8}{1836}$. Thus if the magnetic moment is μ and the nuclear
spin I, then $\mu = I \cdot g(I)$, providing the correct units are
employed. μ is expressed in theoretical proton magnetons
$\frac{eh}{4\pi Mc}$, that is to say, the Bohr electron magneton divided
by the nuclear mass M. By analogy with the electron g
value, one expects for a proton that $I = \frac{1}{2}$ and $\mu = 1$, so
that $g(I)$ would be 2. Experiment, however, shows that μ
for the proton is 2·79, so that $g(I) = 5·58$. (Precision values
are discussed later.)

The magnetic deflection method of calculating the mag-
netic moments has been used in a number of cases. It is
very important, since it is a direct method, and it is to be
hoped that it will be extended in the near future.

Calculation of nuclear magnetic moments

The calculation of nuclear magnetic moments from the
data of hyperfine structure has been given by Goudsmit.[4]
As we have already seen, the coupling energy between
electron and nucleus determines the total splitting, and
this is given by

$$W = A \cdot IJ \cdot \cos(IJ) = \tfrac{1}{2}A[F(F + 1) \\ - J(J + 1) - I(I + 1)].$$

When an alkali-like spectrum (a single optical electron) is
under consideration, then the interval factor A is that of the
optical electron a.

Coupling theory shows that

$$a = \frac{R\alpha^2 z^3}{n^3(1 + \tfrac{1}{2})j(j + 1)} \cdot \frac{g(I)}{1836} \text{ cm.}^{-1}.$$

In this formula R is Rydberg's constant, α^2 is the spectroscopic doublet constant, z is the nuclear charge, n the total quantum number, l and j have the usual significance, and $g(I)$ is the numerical ratio of the magnetic to mechanical moments.

When the case of a penetrating electron is considered, the formula is altered and a relativity correction has to be applied. The final formula for the $g(I)$ factor in the case of a penetrating s electron is

$$g(I) = \frac{a \cdot n_0{}^3 \cdot 1836}{8R\alpha^2 \cdot Z_i z_0{}^2 \cdot K(jZ_i)}.$$

It will be seen that only two changes have really been made. n_0 is the effective total quantum number of the term, which is easily obtained if the absolute term value is known. z^3 has now been replaced by $Z_i z_0{}^2$, in which z_0 is the effective nuclear charge in the outer portion of the electronic orbit and Z_i is the average effective nuclear charge when the electron is passing through the inner penetrating portion of the orbit. For a neutral atom $z_0 = 1$, for a singly ionised atom $z_0 = 2$, etc. In heavy atoms and deeply penetrating orbits the electron approaches so closely to the nucleus that practically all the screening effect of the outer electrons is reduced to zero. The effective Z_i may thus be taken as approximately equal to the atomic number. The relativity correction $K(jZ_i)$ depends upon j and Z_i, and a table of values for K has been calculated by Goudsmit.

As an example of applying the formula, the following [5] calculation of the $g(I)$ factor of tin will now be given.

The nuclear spin of tin is $\frac{1}{2}$ and the $6s \cdot {}^2S_{1/2}$ term (odd isotopes) is a doublet $0 \cdot 207$ cm.$^{-1}$ wide. The F values of the hyperfine structure levels are 1 and 0, so that the separation is the interval factor. Hence

$$A = a = - \, 0 \cdot 207 \text{ cm.}^{-1}.$$

The n_0 for $6s \cdot {}^2S_{1/2}$ in tin is $2 \cdot 685$, and R $= 109,737$. The effective inner charge Z_i is 50, which is the atomic number of tin, and as the Sn II spectrum is under consideration,

$z_0 = 2$. The relativity correction for $j = \frac{1}{2}$ and $Z_i = 50$ is $1\cdot30$, and the spectroscopic doublet constant has the value $5\cdot305 \times 10^{-5}$. On substituting these data, one obtains $g(I) = -1\cdot78$. Since $I = \frac{1}{2}$, and as $\mu = I \cdot g(I)$, the nuclear magnetic moment is $-0\cdot89$ Bohr proton magnetons, or $\frac{1}{2000}$ that of the electron.

The formula utilised above is only to be used with s electrons, and when other relatively non-penetrating orbits are studied a different formula is required, and has been deduced by Goudsmit as follows :—

$$g(I) = \frac{a Z_i j(j+1)(1+\frac{1}{2})}{\Delta\nu \cdot 1(1+1)} \cdot \frac{\lambda(1Z_i)}{K(jZ_i)} \cdot 1836.$$

$g(I)$, a, Z_i, j, 1, K, have their previous meanings ; $\lambda(1Z_i)$ is a relativity correction depending upon the 1 value, i.e. on whether p, d, or f electrons are involved. $\Delta\nu$ is the spin doublet separation. Thus, if a $6p$ electron is under review, then $\Delta\nu$ is the separation between $6p \cdot {}^2P_{3/2}$ and $6p \cdot {}^2P_{1/2}$, and similarly for other electrons. With p electrons, Z_i is not equal to the atomic number Z, but throughout the periodic table it has always been found that

$$Z_i \coloneqq Z - 4.$$

As this is always a little uncertain, the $g(I)$ values calculated from p electrons may be too small.

When the terms arise from complex electron configurations, the separate electron interval constants must be obtained before the $g(I)$ factor can be calculated. Uncertainty often arises here, so that many calculated $g(I)$ factors are only approximate.

Nuclear magnetic moments observed

The known nuclear magnetic moments are shown in the preceding chapter in Table VIII which give the known nuclear spins. A comprehensive list of data has thus now been accumulated. Magnetic moments have been derived in many cases by two independent methods, namely (1) magnetic deflection of molecular and atomic beams, (2)

hyperfine structure measurements. Where results are obtained by both methods, agreement is effectively complete. The precision and certainty in the magnetic deflection experiments are far superior to those in the spectroscopic observations. The information given refers to the normal state only, but suffices to give both mechanical and magnetic moments.

There are broad distinctions between the nuclear magnetic moments of the various classes A, B, C, D, of Table VIII. In class A the moments distribute from 2·7896 downwards. Of particular importance is the large value for the proton. This has been explained theoretically in terms of the Yukawa theory of the meson. According to this, a proton can be regarded as partially dissociated for a small fraction of its life-time into a neutron and positive meson. The latter having a mass of less than one-tenth that of the proton has a correspondingly larger magnetic moment. Thus the mean magnetic moment of the combination exceeds the Bohr magneton.

In class B the most striking feature is the existence of so many *negative magnetic moments*. The only possible explanation is that the magnetic moment of the neutron is itself negative. This again is explicable on the Yukawa theory as shown in discussing class C. Class C is of considerable interest.

The D^2 nucleus has a spin of 1 and as there is considerable independent evidence that proton and neutron have each a spin of $\frac{1}{2}$, clearly the two spins add in parallel. But the magnetic moment of D^2 is much less than that of H (0·8565 compared with 2·7896).[3] One must conclude that the magnetic moment of the neutron is negative, i.e. that it acts in an opposite direction relative to that of the mechanical spin in the case of H.

Since a neutron is uncharged, the spin of such a particle should *apparently have no magnetic moment*. The Yukawa dissociation theory avoids the difficulty. A neutron is partially dissociated for a fraction of its life-time into a proton and a negative meson and as the magnetic moment of the latter is greater than that of the proton, there remains

a residual mean negative magnetic moment for the neutron as a whole.

Clearly of some considerable importance is the fact that Li^6, B^{10}, N^{14}, each probably built out of alpha particles and an added proton-neutron pair, show a regular decrease in magnetic moment.[6]

In class D, nuclear spin is zero and there appears to be no reason for supposing that there exists *any* magnetic moment.

Various theories of nuclear magnetic moment have been proposed. One theory attributes the moment largely to that of single (or odd) nuclear protons or neutrons. The theories, however, are as yet not sufficiently developed to justify their inclusion in a book of this nature.

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NUCLEAR ELECTRIC QUADRUPOLE MOMENT

Deviations from interval rule

It has been found that deviations from the interval rule may arise through electrostatic interaction between a nucleus and the outer electrons. In 1932 Tolansky[1] reported a marked break-down in the cosine interaction law for a term in the As II spectrum. Other cases were found, and in 1935 Schüler and Schmidt[2] correctly interpreted such deviations from the interval rule as showing the existence of *an asymmetrical nuclear electric charge distribution*. This method of studying such nuclear effects is clearly one of much importance to future nuclear theories, and will be dealt with in the following.

Schüler and Schmidt pointed out that the interval rule, represented by $E = A_0 + A' \cos IJ$ *fails and must be replaced* by an expression which is

$$E = A_0 + A' \cos IJ + B' \cos {}^2IJ$$

This becomes equivalent when substitutions are made to
$E = a_0' + \tfrac{1}{2}a'C + b'C($

$$C = F(F + 1) - I(I + 1)$$

In this expression, a_0', a' and b' are constants, a_0' being the displacement of the centre of gravity from the position the term would occupy if the spin were zero, a' is the hyperfine structure interval factor and b' is a measure of the deviation from the interval rule and is also a measure of the nuclear quadrupole moment.

The separations produced by the electrostatic interaction of nucleus and electrons can be shown to be of the form

$$- P \cdot Q \cdot \frac{(\tfrac{3}{8})C(C + 1) - \tfrac{1}{2}IJ(I + 1)(J + 1)}{IJ(2I - 1)(2J + 1)}\cdot{}\cdot$$

The quantity **P** is a measure of the deviation from spherical symmetry of the charge density of the *electrons*. It is zero for a spherically symmetrical distribution. (This is characteristic of any S state.) It is positive for a prolate distribution and negative for an oblate distribution in the direction of angular momentum.

In like manner **Q** *is an average over the charge density of the nucleus*. It is positive or negative according as the nucleus is prolate or oblate in the direction of its angular momentum. **Q** *is called the electric quadrupole moment of the nucleus*.

In conformity with the preceding formulæ, it is found by observation that the perturbation of a hyperfine structure level depends upon the **F** value of that level. To discuss further the nuclear-electron interaction, it is necessary to consider very briefly the wave-mechanics model of electron distribution.

Wave-mechanics model

It is now firmly established that the concept of the electron as a small spherical unit of electricity is only a rough approximation and it has been found necessary to replace the over-simplified idea of Bohr orbits by " eigen-functions ". These can effectively be considered as expressions describing the distribution of electrical density representing the equivalent of the electron. Ultimately it is as if the small " billiard ball " electron model were replaced by a *smeared out* or blurred electrical charge distribution which has maxima of probability at distances from the nucleus corresponding to what were formerly the Bohr orbital radii.

The equivalent electrical distributions for **S**, **P**, **D**, etc., states have been evaluated and it appears that *only* **S** *terms have a spherically symmetrical charge distribution*, whilst **P**, **D**, etc., terms are marked by *unsymmetrical* distribution.

Suppose there is interaction between a non-spherically symmetrical nucleus and a non-spherical electron charge distribution, then, as Schüler and Schmidt first pointed out, there will be a break-down in the interval rule, as shown by Fig. 26 which illustrates two cases.

In the diagram IA and IIA schematically exhibit the manner in which the smeared out wave-mechanical equivalent of the electron distribution can depend on the relative direction of the J axis of the term. The figures are sections, for the distribution in space is rotation symmetric about the J axis shown by the arrow. The two cases correspond to the maximum electric density of the eigen-functions being respectively perpendicular and parallel to J. For a one electron term IA applies to the case when L and J are *parallel* and IIA when L and J are *perpendicular*.
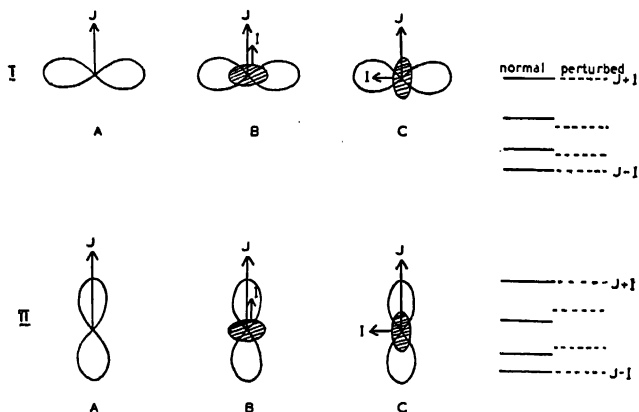
FIG. 26.—Origin of deviation from the interval rule.

Suppose we postulate that the nucleus (shaded in B and C) is *not spherically symmetrical* also and let it be in the form of a rotation ellipsoid whose axis of rotation is the direction of the nuclear spin I. Then Figs. I (B) and II (B) show the situation when I and J are parallel (F is a maximum) and I (C) and II (C) when I and J are perpendicular. When I and J are anti-parallel, the effect is identical with that when I and J are parallel.

From energy considerations the *levels for which the overlap of the electron and nuclear distributions is greatest will be the higher*. Thus I (B) lies higher than I (C) and II (B)

lies deeper than **II (C)**. **B** then corresponds to both the highest and lowest levels in a hyperfine structure pattern and **C** to an intermediate level. It follows that in Case I the intermediate levels displace *downwards* relative to the outer levels and in Case II *upwards*. This is illustrated by the levels at the extreme right.

Break-down of interval rule

Clearly, such displacements lead to the break-down of the interval rule. They can often be fitted into a quadratic formula of the type described above, but there are discrepancies in many cases. When the formula is reasonably fitted the constants a' and b' can be derived. Casimir[3] has shown that the constant b' is related to the quadrupole moment Q such that

$$Q = \frac{b' 8I(2I - 1)J(2J - 1)}{3e^2 P}$$

where e is the electronic charge, and the quantity P is calculable, depending on the particular term. Thus

$$P = \frac{Z_i Z_0 K}{n^{*3} L(L + \frac{1}{2})(L + 1)}$$

in which K is a calculable constant, e.g. $-\frac{1}{6}$ for $^3D_1 - \frac{4}{7}$ for $^3D_3$, etc. The symbols Z_i, Z_0, n^* are as used in earlier chapters.

Numerical substitution from results show that Q can vary from o to 5×10^{-24} cm.^{2} from which it appears that the deviation from spherical symmetry is a matter of at most a few per cent. (Casimir).[3]

There exists some doubt about many of the reported values for nuclear electric quadrupole moment. It is clear that many causes can lead to spurious values. Thus bad measurement, differential absorption effects, incipient electric and magnetic field perturbation, neighbouring level perturbation, and even photographic developer effects, can all give rise to a spurious break-down in the interval rule, and make a false quadrupole moment appear. It is

perhaps significant that often two terms in a spectrum give different values of the quadrupole moment and indeed one case had been reported in which the apparent nuclear quadrupole moment is positive from one term and negative from another, clearly a serious inconsistency and strong evidence of the existence of external perturbation as the cause, and not quadrupole moment.

The quadrupole moments reported so far are given in the table below, the units being 10^{-24} cm.^{2}. They have been collected from a number of sources.

Electrical nuclear quadrupole moments

TABLE IX
REPORTED ELECTRICAL NUCLEAR QUADRUPOLE MOMENTS

Atom.	Mass.	Charge.	Spin.	Magnetic Moment.	Quadrupole Moment $\times 10^{-24}$ cm.^{2}
Cu	63	29	$\frac{3}{2}$	+ 2·5	− 0
Cu	65	29	$\frac{3}{2}$	+ 2·6	− 0
Ga	69	31	$\frac{3}{2}$	+ 2·0	+ 1
Ga	71	31	$\frac{3}{2}$	+ 2·5	0 ± 0·5
As	75	33	$\frac{3}{2}$	+ 1·5	+ 0·3
Kr	83	36	$\frac{9}{2}$	− 1·0	+ 0·15
In	115	49	$\frac{9}{2}$	+ 5·5	+ 0·8
I	127	53	$\frac{5}{2}$	+ 2·8	− 0·5
Xe	131	54	$\frac{3}{2}$	− 0·8	0 ± 0·1
Eu	151	63	$\frac{5}{2}$	+ 3·4	+ ∼ 1·2
Eu	153	63	$\frac{5}{2}$	+ 1·5	+ ∼ 2·5
Yb	171	70	$\frac{1}{2}$	+ 0·4	−
Yb	173	70	$\frac{5}{2}$	− 0·7	+ 3·9
Cp	175	71	$\frac{7}{2}$	∼ + 2·6	+ 5·9
Re	185	75	$\frac{5}{2}$	+ 3·3	+ 2·8
Re	187	75	$\frac{5}{2}$	+ 3·3	+ 2·6
Hg	201	80	$\frac{3}{2}$	− 0·6	+ 0·5
Bi	209	83	$\frac{9}{2}$	+ 3·6	− 0·4

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[3] Casimir, Prize Essay, Teyler's Tweede Genootschap, Haarlem, 1936.

HYPERFINE STRUCTURE—ZEEMAN EFFECT

THIS will be only described very briefly, more detail being available elsewhere.[1] The complete Paschen-Back effect is the simplest to consider. In this, the external magnetic field is so strong that its coupling with I and J is great enough to break the mutual interaction of I and J. It can be shown that, to a first approximation, the Zeeman pattern is the same as that of an atom when no nuclear spin is considered, that is to say, the line will be split up into its usual Zeeman components. The introduction of a nuclear spin affects each of these Zeeman components slightly and this can sometimes be detected. The total interaction energy of the atom with the field H is

$$w = O[m_I . g(I) + m_J \, g] + A . IJ . \cos (IJ),$$

where O is the Lorentz unit $\dfrac{ehH}{4\pi m_0 c}$, g is the ordinary electronic g factor, $g(I)$ the nuclear factor, and m_I and m_J the projections of I and J along H. Averaging the cosine term reduces the expression to

$$m_J(Og + Am_I).$$

m_I can assume any of the $2I + 1$ integral or half integral values between $+ I$ and $- I$. Hence, each Zeeman *level*, which without the spin is single, now splits up into $2I + 1$ components equally spaced by the distance Am_J. The only transitions allowed are those in which m_I does not change, so that each gross Zeeman *line* splits into $2I + 1$ hyperfine structure Zeeman *lines*. For two terms J and J' the separations will be $Am_J - A'm_{J'}$. The A and A' values can be calculated from the hyperfine structures which arise when there is no magnetic field, and m_J is $+ \frac{1}{2}$ or $-\frac{1}{2}$ for both states when parallel components are ob-

served. Hence, the separation can be predicted. The number of components gives the simplest and most satisfactory way of obtaining the nuclear spin. Thus, in Bi I, where the Zeeman theory was beautifully verified, each gross Zeeman component consisted of 10 lines. As this is $2I + 1$, then $I = \frac{9}{2}$.

If incomplete Paschen-Back effects exist, the pattern becomes extremely complicated, but the experimental evidence seems to agree very well with theory, even to the extent that the normally forbidden transitions occur as is to be expected when external fields are applied.

REFERENCES

[1] For details of the theory of Zeeman effect in hyperfine structure see Pauling and Goudsmit, " Structure of Line Spectra " ; also Goudsmit and Bacher, *Zeit. f. Phys.*, 66, 13, 1930, and *Phys. Rev.*, 35, 1929, 1930.

LANDÉ'S PARTICLE THEORY OF NUCLEAR SPIN

LANDÉ [1] has proposed that the nuclear spin of an odd weight atom may be due to the single odd particle, respectively a proton and neutron in types A and B of Table VIII (see before). Consider first odd-proton nuclei. The unbound odd proton is considered to have a spin $s = \frac{1}{2}$ and an orbital angular moment 1. These combine vectorially to a resultant I which is the *nuclear spin*. Thus I may be either $1 + \frac{1}{2}$ or $1 - \frac{1}{2}$. From this Landé derives a formula for $g(I)$ which is

$$g(I) = g_l \left[\frac{l(l + 1) + I(I + 1) - s(s + 1)}{2I(I + 1)} \right]$$
$$+ g_s \left[\frac{s(s + 1) + I(I + 1) - l(l + 1)}{2I(I + 1)} \right]$$

in which $s = \frac{1}{2}$, the proton spin, $g_l = 1$ and g_s the magnetic factor of the proton. By taking $g_s = 4$, Landé was able to obtain an approximate fit between observed and calculated $g(I)$ values, for I can only arise from one of two adjacent 1 values and the $g(I)$ nearest to that observed can be adopted. However, it is now clear that the approximate fits obtained are probably largely accidental, since g_s is known with certainty to be much more than 4, in fact 5·58 (see Table VIII, magnetic moment of proton).

The above theory was extended to include the odd-neutron case and g_l was postulated zero, since the neutron was considered to have no magnetic moment due to orbital motion. Observations were best fitted by adopting $g_s = -1·2$, giving the neutron a *negative* magnetic moment of $-0·6$ magnetons. This value leads to both positive and negative $g(I)$ factors, as indeed are found experimentally. Agreement is, however, but partial, and Tamm and Altschuler [2] consider that sometimes a pair of neutrons

does not form a closed shell of zero spin, but add up to a spin of 1. This spin combines with the remaining odd neutron (or proton) and if the former, the combined spin will be $\frac{3}{2}$. This assumption doubles the possible number of $g(\mathrm{I})$ factors that can be calculated for a single nuclear spin and thus introduces further uncertainty.

Thus, whilst the theory that the spin is due to one particle (or at most three particles) is clearly of considerable interest, accounting as it does for the small observed spins, yet it cannot be considered to have established itself as yet.

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[2] Tamm and Altschuler, *Ac. U.S.S.R.*, **1**, 455, 1934

INDEX